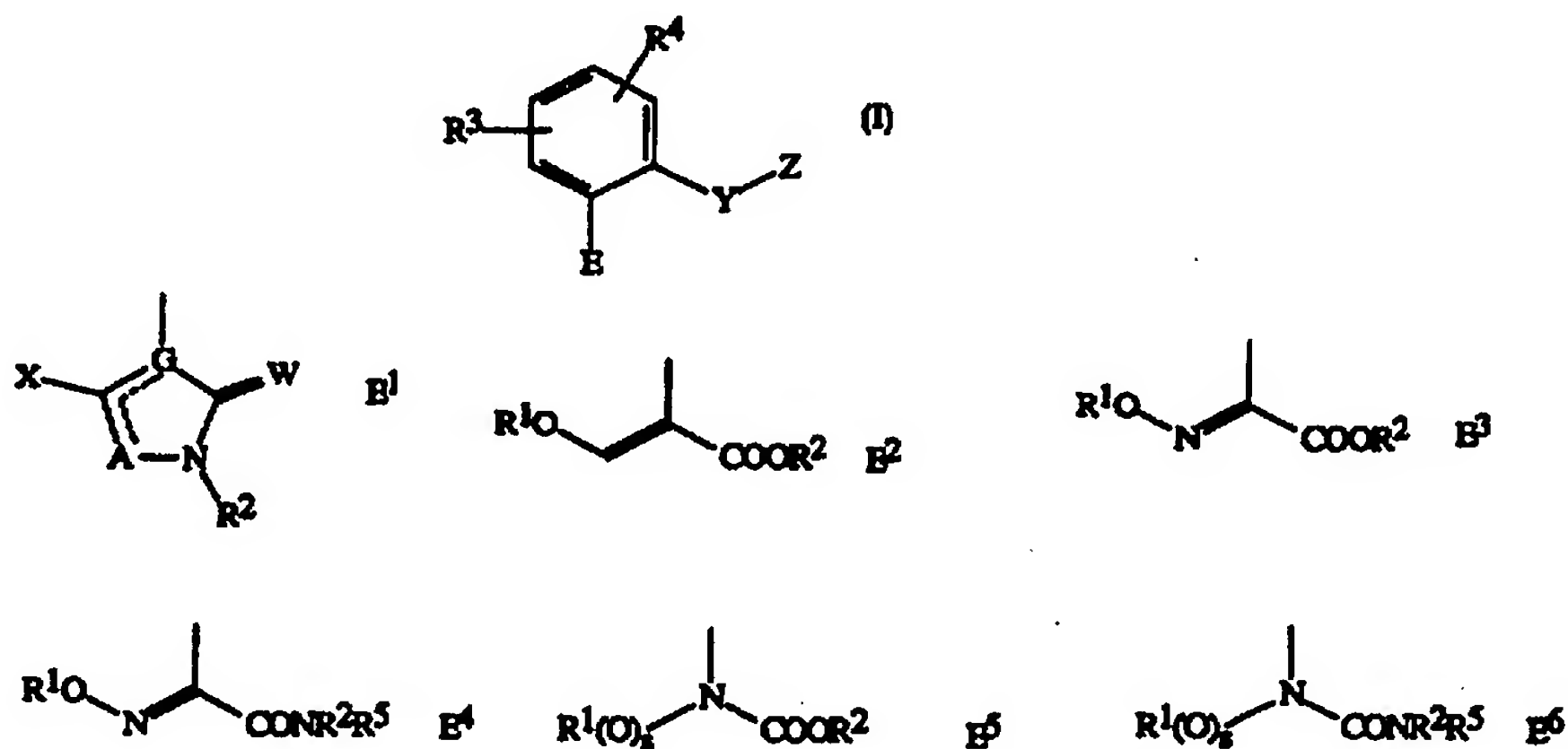




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(54) Title: ARTHROPODICIDAL AND FUNGICIDAL ORGANOSILANES AND ORGANOGERMANES



(57) Abstract

Compounds of formula (I), and their *N*-oxides and agriculturally-suitable salts, are disclosed which are useful as fungicides and arthropodicides, wherein E is E¹, E², E³, E⁴, E⁵ or E⁶; and A, G, W, X, R¹, R², R³, R⁴, R⁵, Y, Z and s are as defined in the disclosure. Also disclosed are compositions containing the compounds of formula (I) and a method for controlling plant diseases caused by fungal plant pathogens which involves applying an effective amount of a compound of formula (I). Also disclosed are compositions containing the compounds of formula (I) and a method for controlling arthropods which involves contacting the arthropods or their environment with an effective amount of a compound of formula (I).

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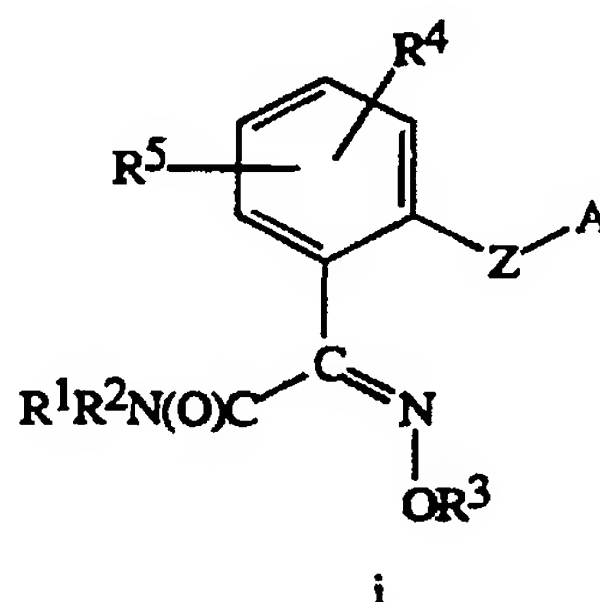
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TITLEARTHROPODICIDAL AND FUNGICIDAL
ORGANOSILANES AND ORGANOGERMANESBACKGROUND OF THE INVENTION

5 This invention relates to certain (hetero)arylsilanes and (hetero)arylgermanes, their *N*-oxides, agriculturally-suitable salts and compositions, and methods of their use as fungicides and arthropodicides.

EP-A-398,692 discloses amides of Formula i as fungicides for crop protection.
Compounds of Formula i are:

10



wherein

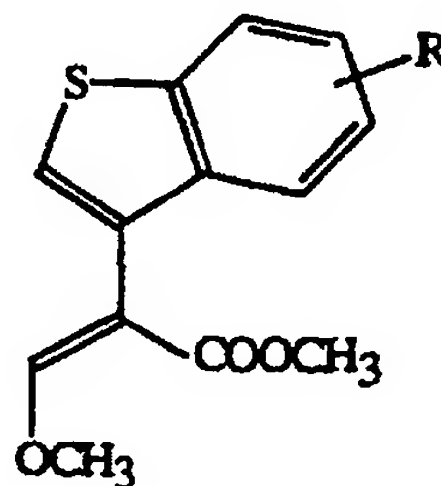
R^1 and R^2 are each hydrogen, lower alkyl, or lower cycloalkyl;

R^3 is lower alkyl, or lower cycloalkyl;

15 A is, *inter alia*, a phenyl group or a heterocyclic group optionally substituted with not more than three substituents chosen from, among others, lower alkyl-substituted silyl; and

Z is, *inter alia*, -O-; -S-; -SO-; -CH₂CH₂-; -CH=CH-; -CH₂O-; -CH₂S-; -CH₂SO-; -OCH₂-; -SCH₂-; or -SOCH₂-.

20 CA 2,032,045 discloses compounds of Formula ii as fungicides for crop protection. Compounds of Formula ii are:



wherein

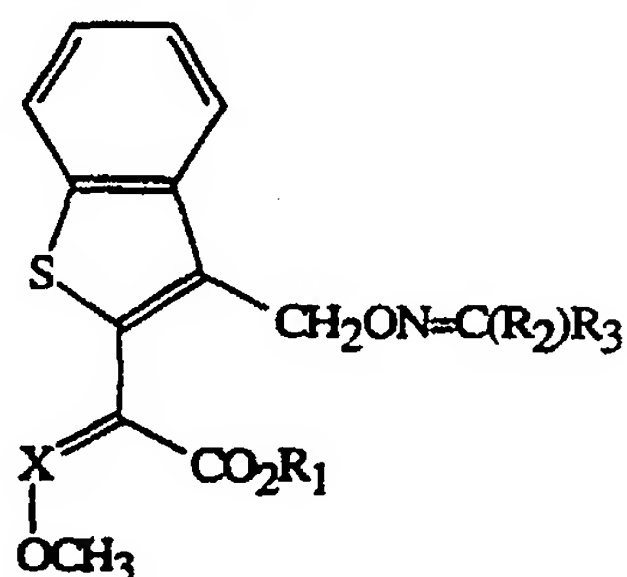
R is, *inter alia*, aryloxy-C₁₋₄-alkyl, heteroaryloxy-C₁₋₄-alkyl, arylthio-C₁₋₄-alkyl, heteroarylthio-C₁₋₄-alkyl, aryloxy, R¹CH=CH, or R⁴R⁵C=NOCH₂;

R¹ is aryl or heteroaryl; and

5 R⁴ and R⁵ are, *inter alia*, aryl or heteroaryl;

and each aryl and heteroaryl group can have one or more substituents selected from, among others, tri(C₁₋₄alkyl)silyl.

WO 93/08183 discloses compounds of Formula iii as fungicides for crop protection. Compounds of Formula iii are:



iii

10

wherein

X is N or CH;

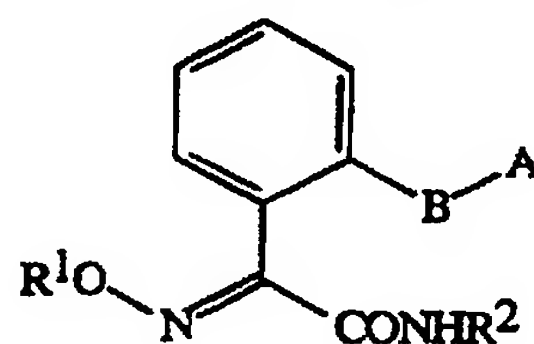
R₁ is C₁-C₄alkyl; and

R₂ and R₃ are, among others, independently C₁-C₄alkyl, halo-C₁-C₄alkyl,

15 C₁-C₄alkoxy, unsubstituted or substituted aryl or heteroaryl group;

and each substituted aryl and heteroaryl group is substituted by one, two or three substituents selected from, among others, trimethylsilyl.

EP-A-596,692 discloses processes to compounds of Formula iv useful as fungicides for crop protection. Compounds of Formula iv are:



iv

20

wherein

A is, *inter alia*, a phenyl group or a heterocyclic group optionally substituted with substituents chosen from, among others, lower alkylsilyl;

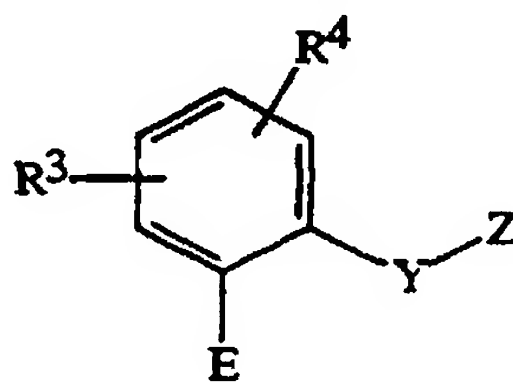
B is, *inter alia*, -O-; -S-; -CH₂CH₂-; -CH=CH-; -C≡C-; -CH₂O-; -CH₂S-; -CH₂SO-; -OCH₂-; -SCH₂-; or -SOCH₂-; and

R¹ and R² are independently H or lower alkyl.

The (hetero)arylsilanes and (hetero)arylgermanes of this invention are not disclosed in these documents.

SUMMARY OF THE INVENTION

This invention is directed to compounds of Formula I including all geometric and stereoisomers, *N*-oxides, and agriculturally suitable salts thereof, agricultural compositions containing them and their use as fungicides and arthropodicides:

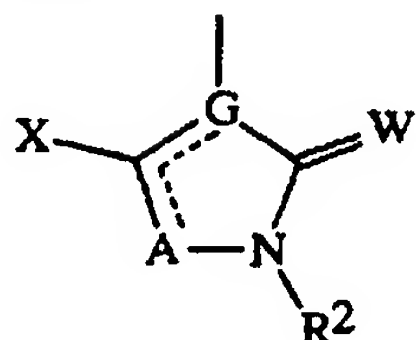


I

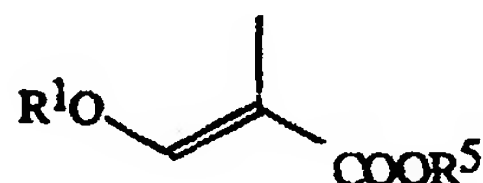
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wherein:

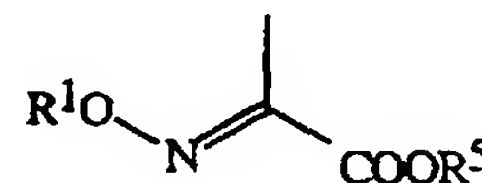
E is



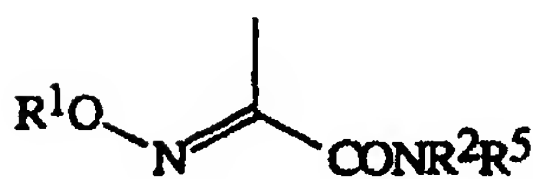
E¹



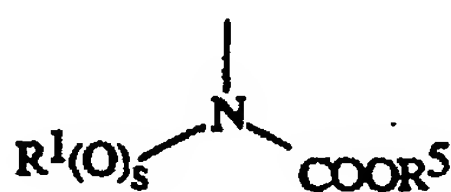
E²



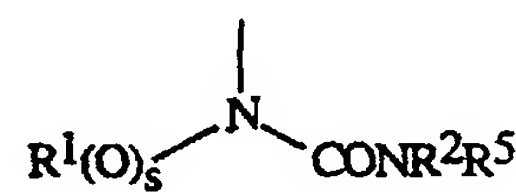
E³



E⁴



E⁵



E⁶

, or

A is O; S; N; NR⁵; or CR¹⁴;

15

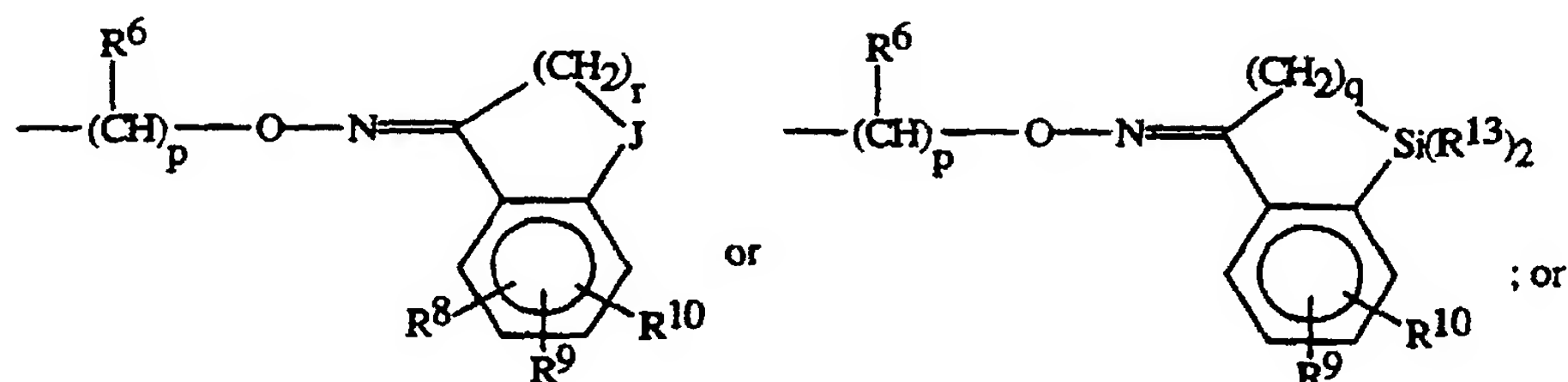
G is C or N; provided that when G is C, A is O, S or NR⁵ and the floating double bond is attached to G; and when G is N, A is N or CR¹⁴ and the floating double bond is attached to A;

W is O; S; NH; N(C₁-C₆ alkyl); or NO(C₁-C₆ alkyl);

X is OR¹; S(O)_mR¹; or halogen;

- R^1 and R^5 are each independently H; C_1 - C_6 alkyl; C_1 - C_6 haloalkyl; C_2 - C_6 alkenyl; C_2 - C_6 haloalkenyl; C_2 - C_6 alkynyl; C_2 - C_6 haloalkynyl; C_3 - C_6 cycloalkyl; C_2 - C_4 alkylcarbonyl; or C_2 - C_4 alkoxycarbonyl;
- 5 R^2 is H; C_1 - C_6 alkyl; C_1 - C_6 haloalkyl; C_2 - C_6 alkenyl; C_2 - C_6 haloalkenyl; C_2 - C_6 alkynyl; C_2 - C_6 haloalkynyl; C_3 - C_6 cycloalkyl; C_2 - C_4 alkylcarbonyl; C_2 - C_4 alkoxycarbonyl; hydroxy; C_1 - C_2 alkoxy; or acetyloxy;
- 10 R^3 and R^4 are each independently H; halogen; cyano; nitro; hydroxy; C_1 - C_6 alkyl; C_1 - C_6 haloalkyl; C_2 - C_6 alkenyl; C_2 - C_6 haloalkenyl; C_2 - C_6 alkynyl; C_2 - C_6 haloalkynyl; C_1 - C_6 alkoxy; C_1 - C_6 haloalkoxy; C_2 - C_6 alkenyloxy; C_2 - C_6 alkynyloxy; C_1 - C_6 alkylthio; C_1 - C_6 alkylsulfinyl; C_1 - C_6 alkylsulfonyl; formyl; C_2 - C_6 alkylcarbonyl; C_2 - C_6 alkoxycarbonyl; $NH_2C(O)$; $(C_1-C_4 \text{ alkyl})NHC(O)$; $(C_1-C_4 \text{ alkyl})_2NC(O)$; $Si(R^{13})_3$; $Ge(R^{13})_3$; $(R^{13})_3Si-C\equiv C-$; or phenyl, phenylethynyl, benzoyl, or phenylsulfonyl each substituted with R^9 and R^{10} ;
- 15 Y is $-O-$; $-S(O)_n-$; $-NR^6-$; $-C(=O)-$; $-CH(OR^6)-$; $-CHR^6-$; $-CHR^6CHR^6-$; $-CR^6=CR^6-$; $-C\equiv C-$; $-CHR^6O-$; $-OCHR^6-$; $-CHR^6S(O)_n-$; $-S(O)_nCHR^6-$; $-CHR^6O-N=C(R^7)-$; $-(R^7)C=N-OCH(R^6)-$; $-C(R^7)=N-O-$; $-O-N=C(R^7)-$; $-CHR^6OC(=O)N(R^{15})-$; or a direct bond; and the directionality of the Y linkage is defined such that the moiety depicted on the left side of the linkage is bonded to the phenyl ring and the moiety on the right side of the linkage is bonded to Z;
- 20 R^6 is independently H or C_1 - C_3 alkyl;
- R^7 is H; C_1 - C_6 alkyl; C_1 - C_6 haloalkyl; C_1 - C_6 alkoxy; C_1 - C_6 haloalkoxy; C_2 - C_6 alkenyl; C_2 - C_6 haloalkenyl; C_2 - C_6 alkynyl; C_2 - C_6 haloalkynyl; C_3 - C_6 cycloalkyl; C_2 - C_4 alkylcarbonyl; C_2 - C_4 alkoxycarbonyl; cyano; or morpholinyl;
- 25 Z is phenyl substituted with R^8 , R^9 , and R^{10} ; or Z is a 5 to 14-membered aromatic heterocyclic ring system selected from the group monocyclic ring, fused bicyclic ring and fused tricyclic ring, each aromatic ring system containing 1 to 6 heteroatoms independently selected from the group nitrogen, oxygen, and sulfur, provided that each aromatic ring system contains no more than 4 nitrogens, no more than 2 oxygens, and no more than 2 sulfurs, each aromatic ring system substituted with R^8 and optionally substituted with one of R^9 , R^{10} , or both R^9 and R^{10} ; or
- 30

Y and Z are taken together to form



R^3 , Y, and Z are taken together with the phenyl ring to form a naphthalene moiety substituted on either ring with R^8 and on either ring with R^4 ;

J is $-\text{CH}_2-$; $-\text{CH}_2\text{CH}_2-$; $-\text{OCH}_2-$; $-\text{CH}_2\text{O}-$; $-\text{SCH}_2-$; $-\text{CH}_2\text{S}-$; $-\text{N}(\text{R}^{16})\text{CH}_2-$; or $-\text{CH}_2\text{N}(\text{R}^{16})-$; each CH_2 group optionally substituted with 1 to 2 CH_3 ;

R^8 is $\text{SiR}^{19}\text{R}^{20}\text{R}^{21}$ or $\text{GeR}^{19}\text{R}^{20}\text{R}^{21}$;

R^9 is H; 1-2 halogen; C_1 - C_6 alkyl; C_1 - C_6 haloalkyl; C_1 - C_6 alkoxy; C_1 - C_6 haloalkoxy; C_2 - C_6 alkenyl; C_2 - C_6 haloalkenyl; C_2 - C_6 alkynyl; C_1 - C_6 alkylthio; C_1 - C_6 haloalkylthio; C_1 - C_6 alkylsulfinyl; C_1 - C_6 alkylsulfonyl; C_3 - C_6 cycloalkyl; C_3 - C_6 alkenyloxy; $\text{CO}_2(\text{C}_1$ - C_6 alkyl); $\text{NH}(\text{C}_1$ - C_6 alkyl); $\text{N}(\text{C}_1$ - C_6 alkyl) $_2$; $-\text{C}(\text{R}^{18})=\text{NOR}^{17}$; cyano; nitro; SF_5 ; $\text{SiR}^{22}\text{R}^{23}\text{R}^{24}$; or $\text{GeR}^{22}\text{R}^{23}\text{R}^{24}$; or R^9 is phenyl, benzyl, benzoyl, phenoxy, pyridinyl, pyridinyloxy, thienyl, thienyloxy, furanyl, pyrimidinyl, or pyrimidinyloxy each substituted with R^{11} and R^{12} ;

R^{10} is H; halogen; C_1 - C_4 alkyl; C_1 - C_4 haloalkyl; C_1 - C_4 alkoxy; nitro; or cyano; or

R^{11} and R^{12} are each independently H; halogen; C_1 - C_4 alkyl; C_1 - C_4 haloalkyl; C_1 - C_4 alkoxy; C_1 - C_4 haloalkoxy; nitro; cyano; $\text{Si}(\text{R}^{13})_3$; or $\text{Ge}(\text{R}^{13})_3$;

R^{13} is independently C_1 - C_4 alkyl;

R^{14} is H; halogen; C_1 - C_6 alkyl; C_1 - C_6 haloalkyl; C_2 - C_6 alkenyl; C_2 - C_6 haloalkenyl; C_2 - C_6 alkynyl; C_2 - C_6 haloalkynyl; or C_3 - C_6 cycloalkyl;

R^{15} , R^{16} , R^{17} , and R^{18} are each independently H; C_1 - C_3 alkyl; or phenyl optionally substituted with halogen, C_1 - C_4 alkyl, C_1 - C_4 haloalkyl, C_1 - C_4 alkoxy, C_1 - C_4 haloalkoxy, nitro or cyano;

R^{19} , R^{20} , R^{21} , R^{22} , R^{23} , and R^{24} are each independently C_1 - C_6 alkyl; C_1 - C_6 alkenyl; C_1 - C_4 alkoxy; or phenyl;

m and n are each independently 0, 1 or 2;

p, r, and s are each independently 0 or 1; and

q is 1 or 2;

provided that when E is E^4 and Y is $-\text{O}-$; $-\text{S}(\text{O})_n-$; $-\text{NR}^6-$; $-\text{C}(=\text{O})-$; $-\text{CH}(\text{OR}^6)-$; $-\text{CHR}^6-$; $-\text{CHR}^6\text{CHR}^6-$; $-\text{CR}^6=\text{CR}^6-$; $-\text{C}\equiv\text{C}-$; $-\text{CHR}^6\text{O}-$; $-\text{OCHR}^6-$; $-\text{CHR}^6\text{S}(\text{O})_n-$; or $-\text{S}(\text{O})_n\text{CHR}^6-$, then R^8 is $\text{GeR}^{19}\text{R}^{20}\text{R}^{21}$.

DETAILED DESCRIPTION OF THE INVENTION

In the above recitations, the term "alkyl", used either alone or in compound words such as "alkylthio" or "haloalkyl" includes straight-chain or branched alkyl, such as, methyl, ethyl, *n*-propyl, *i*-propyl, or the different butyl, pentyl or hexyl isomers.

- 5 "Alkenyl" includes straight-chain or branched alkenes such as vinyl, 1-propenyl, 2-propenyl, and the different butenyl, pentenyl and hexenyl isomers. "Alkenyl" also includes polyenes such as 2,4-hexadienyl. "Alkynyl" includes straight-chain or branched alkynes such as ethynyl, 1-propynyl, 2-propynyl and the different butynyl, pentynyl and hexynyl isomers. "Alkynyl" can also include moieties comprised of multiple triple bonds
10 such as 2,5-hexadiynyl. "Alkoxy" includes, for example, methoxy, ethoxy, *n*-propyloxy, isopropyloxy and the different butoxy, pentoxy and hexyloxy isomers. "Alkenyloxy" includes straight-chain or branched alkenyloxy moieties. Examples of alkenyloxy include $\text{H}_2\text{C}=\text{CHCH}_2\text{O}$, $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{O}$, $(\text{CH}_3)\text{CH}=\text{CHCH}_2\text{O}$, $(\text{CH}_3)\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2\text{O}$ and $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{O}$. "Alkynyloxy" includes straight-chain or branched alkynyloxy
15 moieties. Examples include $\text{HC}\equiv\text{CCH}_2\text{O}$, $\text{CH}_3\text{C}\equiv\text{CCH}_2\text{O}$ and $\text{CH}_3\text{C}\equiv\text{CCH}_2\text{CH}_2\text{O}$. "Alkylthio" includes branched or straight-chain alkylthio moieties such as methylthio, ethylthio, and the different propylthio, butylthio, pentylthio and hexylthio isomers. "Alkylsulfinyl" includes both enantiomers of an alkylsulfinyl group. For example, $\text{CH}_3\text{S}(\text{O})$, $\text{CH}_3\text{CH}_2\text{S}(\text{O})$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{S}(\text{O})$, $(\text{CH}_3)_2\text{CHS}(\text{O})$ and the different
20 butylsulfinyl, pentylsulfinyl and hexylsulfinyl isomers. Examples of "alkylsulfonyl" include $\text{CH}_3\text{S}(\text{O})_2$, $\text{CH}_3\text{CH}_2\text{S}(\text{O})_2$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{S}(\text{O})_2$, $(\text{CH}_3)_2\text{CHS}(\text{O})_2$ and the different butylsulfonyl, pentylsulfonyl and hexylsulfonyl isomers. "Cycloalkyl" includes, for example, cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl. The term "aromatic heterocyclic ring system" includes fully aromatic heterocycles and heterocycles in which
25 at least one ring of a polycyclic ring system is aromatic.

- The term "halogen", either alone or in compound words such as "haloalkyl", includes fluorine, chlorine, bromine or iodine. The term "1-2 halogen" indicates that one or two of the available positions for that substituent may be halogen. Further, when used in compound words such as "haloalkyl", said alkyl may be partially or fully substituted
30 with halogen atoms which may be the same or different. Examples of "haloalkyl" include F_3C , ClCH_2 , CF_3CH_2 and CF_3CCl_2 . The terms "haloalkenyl", "haloalkynyl", "haloalkoxy", and the like, are defined analogously to the term "haloalkyl". Examples of "haloalkenyl" include $(\text{Cl})_2\text{C}=\text{CHCH}_2$ and $\text{CF}_3\text{CH}_2\text{CH}=\text{CHCH}_2$. Examples of "haloalkynyl" include $\text{HC}\equiv\text{CCHCl}$, $\text{CF}_3\text{C}\equiv\text{C}$, $\text{CCl}_3\text{C}\equiv\text{C}$ and $\text{FCH}_2\text{C}\equiv\text{CCH}_2$. Examples
35 of "haloalkoxy" include CF_3O , $\text{CCl}_3\text{CH}_2\text{O}$, $\text{HCF}_2\text{CH}_2\text{CH}_2\text{O}$ and $\text{CF}_3\text{CH}_2\text{O}$. Examples of "haloalkylthio" include CCl_3S , CF_3S , $\text{CCl}_3\text{CH}_2\text{S}$ and $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{S}$.

The total number of carbon atoms in a substituent group is indicated by the " $\text{C}_i\text{-C}_j$ " prefix where *i* and *j* are numbers from 1 to 6. For example, $\text{C}_1\text{-C}_3$ alkylsulfonyl

designates methylsulfonyl through propylsulfonyl. Examples of "alkylcarbonyl" include $C(O)CH_3$, $C(O)CH_2CH_2CH_3$ and $C(O)CH(CH_3)_2$. Examples of "alkoxycarbonyl" include $CH_3OC(=O)$, $CH_3CH_2OC(=O)$, $CH_3CH_2CH_2OC(=O)$, $(CH_3)_2CHOC(=O)$ and the different butoxy- or pentoxycarbonyl isomers. In the above recitations, when a
5 compound of Formula I is comprised of one or more pyridinyl or pyrimidinyl rings, all substituents are attached to these heterocycles through the carbon atom(s) of the moieties.

When a group contains a substituent which can be hydrogen, for example R^3 or R^9 , then, when this substituent is taken as hydrogen, it is recognized that this is
10 equivalent to said group being unsubstituted.

Compounds of this invention can exist as one or more stereoisomers. The various stereoisomers include enantiomers, diastereomers, atropisomers and geometric isomers. One skilled in the art will appreciate that one stereoisomer may be more active and/or may exhibit beneficial effects when enriched relative to the other stereoisomer(s) or when
15 separated from the other stereoisomer(s). Additionally, the skilled artisan knows how to separate, enrich, and/or to selectively prepare said stereoisomers. Accordingly, the present invention comprises compounds selected from Formula I, *N*-oxides and agriculturally suitable salts thereof. The compounds of the invention may be present as a mixture of stereoisomers, individual stereoisomers, or as an optically active form.

20 The salts of the compounds of the invention include acid-addition salts with inorganic or organic acids such as hydrobromic, hydrochloric, nitric, phosphoric, sulfuric, acetic, butyric, fumaric, lactic, maleic, malonic, oxalic, propionic, salicylic, tartaric, 4-toluenesulfonic or valeric acids. The salts of the compounds of the invention also include those formed with organic bases (e.g., pyridine, ammonia, or triethylamine)
25 or inorganic bases (e.g., hydrides, hydroxides, or carbonates of sodium, potassium, lithium, calcium, magnesium or barium) when the compound contains an acidic group such as a phenol.

Of note are embodiments where R^1 , R^2 , and R^5 are each independently H; C_1 - C_6 alkyl; C_1 - C_6 haloalkyl; C_2 - C_6 alkenyl; C_2 - C_6 haloalkenyl; C_2 - C_6 alkynyl; C_2 - C_6
30 haloalkynyl; C_3 - C_6 cycloalkyl; C_2 - C_4 alkylcarbonyl; or C_2 - C_4 alkoxy carbonyl.

For R^2 , preferred alkyl groups include C_1 - C_3 alkyl; preferred haloalkyl groups include C_1 - C_3 haloalkyl; preferred alkenyl groups include allyl; preferred haloalkenyl groups include haloallyl; preferred alkynyl groups include propargyl; preferred haloalkynyl groups include halopropargyl; and preferred cycloalkyl groups include
35 cyclopropyl.

Also of note are embodiments where W is O or S; embodiments where R^3 and R^4 are each independently H, halogen, cyano, nitro, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, C_2 - C_6 alkenyl, C_2 - C_6 haloalkenyl, C_2 - C_6 alkynyl, C_2 - C_6 haloalkynyl, C_1 - C_6 alkoxy, C_1 - C_6

haloalkoxy, C₂-C₆ alkenyloxy, C₂-C₆ alkynyloxy, or phenyl substituted with R⁹ and R¹⁰; embodiments where R⁹ is other than SF₅; and embodiments where R¹⁹, R²⁰, R²¹, R²², R²³, and R²⁴ are each independently C₁-C₆ alkyl, C₁-C₄ alkoxy, or phenyl.

Preferred compounds for reasons of better activity and/or ease of synthesis are:

- 5 Preferred 1. Compounds of Formula I above, and *N*-oxides and agriculturally-suitable salts thereof, wherein:

W is O when E is E¹;

R¹ is C₁-C₃ alkyl or C₁-C₃ haloalkyl;

R² is H; C₁-C₃ alkyl; C₁-C₃ haloalkyl; or cyclopropyl;

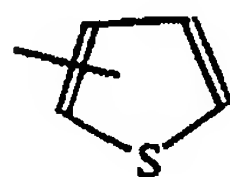
10 R³ and R⁴ are each independently H; halogen; cyano; nitro; C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₁-C₆ alkoxy; or C₁-C₆ haloalkoxy;

Y is -O-; -CH=CH-; -CH₂O-; -OCH₂-; -CH₂S(O)_n-; -CH₂O-N=C(R⁷)-; -C(R⁷)=N-O-; -CH₂OC(O)NH-; or a direct bond;

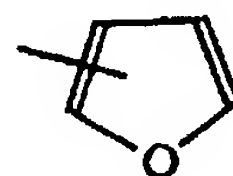
15 R⁷ is H; C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₂-C₆ alkenyl; C₂-C₆ alkynyl;

C₃-C₆ cycloalkyl; or cyano;

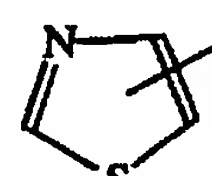
Z is phenyl substituted with R⁸, R⁹, and R¹⁰; or Z is



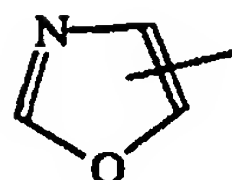
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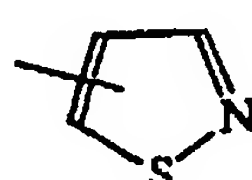
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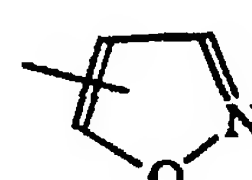
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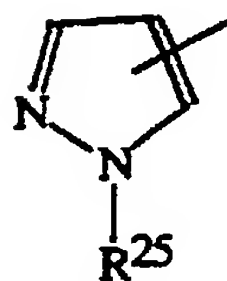
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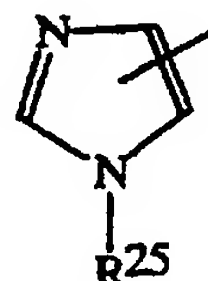
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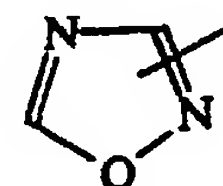
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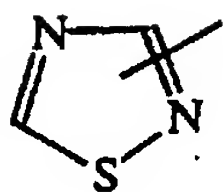


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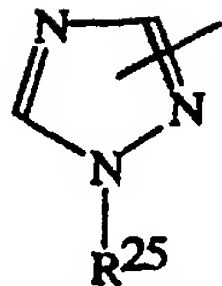


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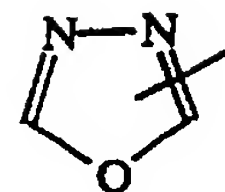
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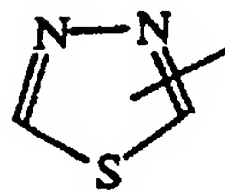
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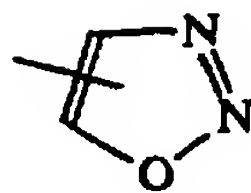
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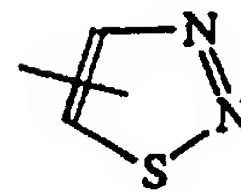
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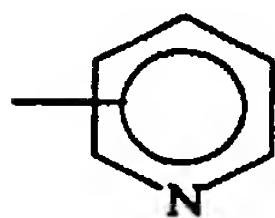
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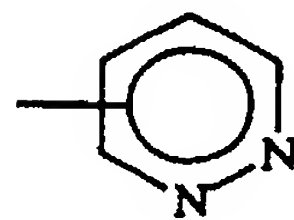
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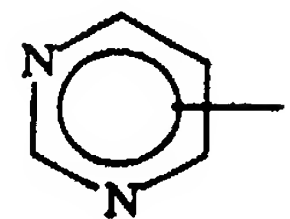
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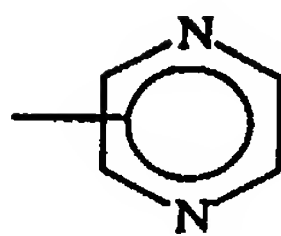
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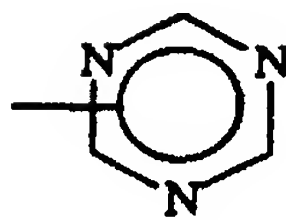
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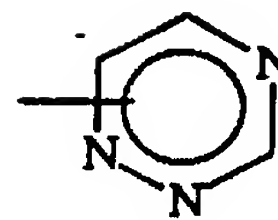
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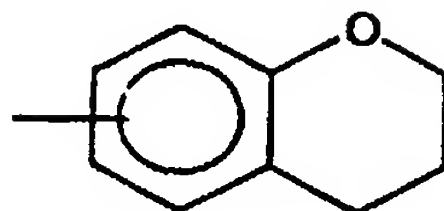
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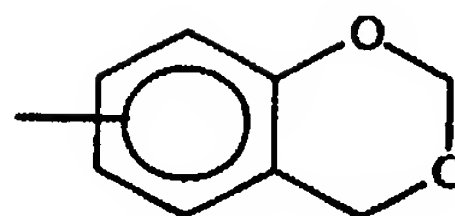
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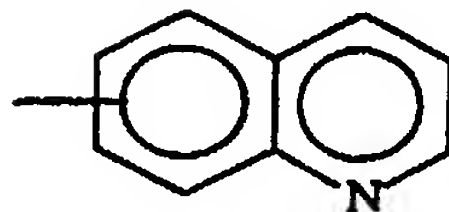
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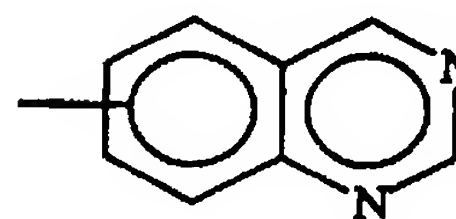
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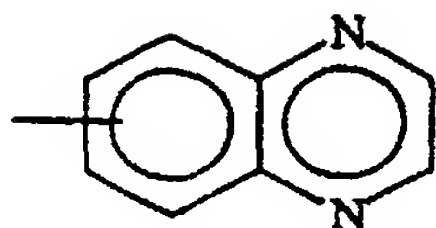


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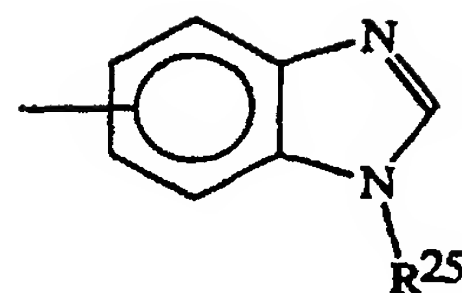


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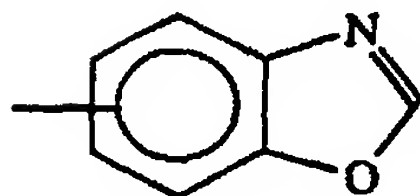
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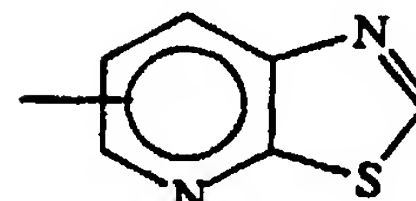
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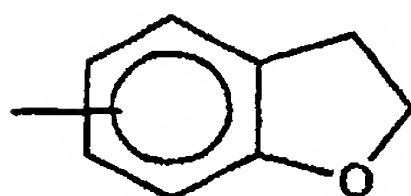
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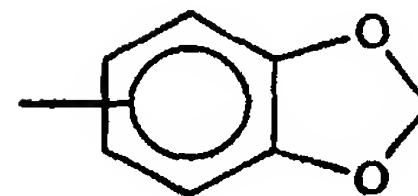
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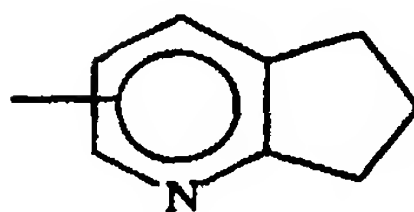
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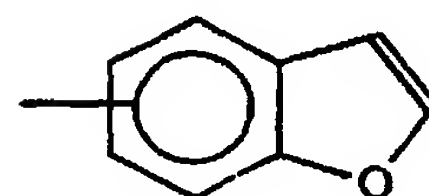
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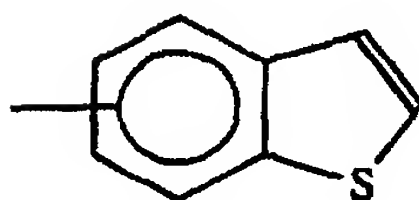
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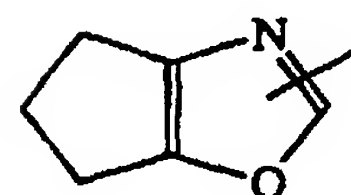
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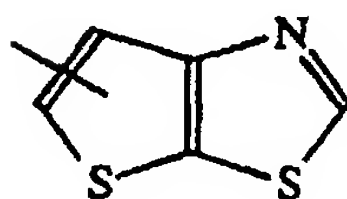
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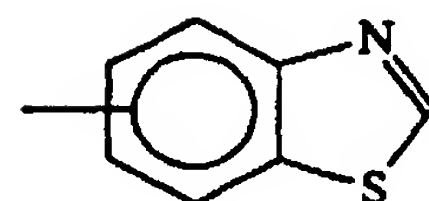


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Z-36

or

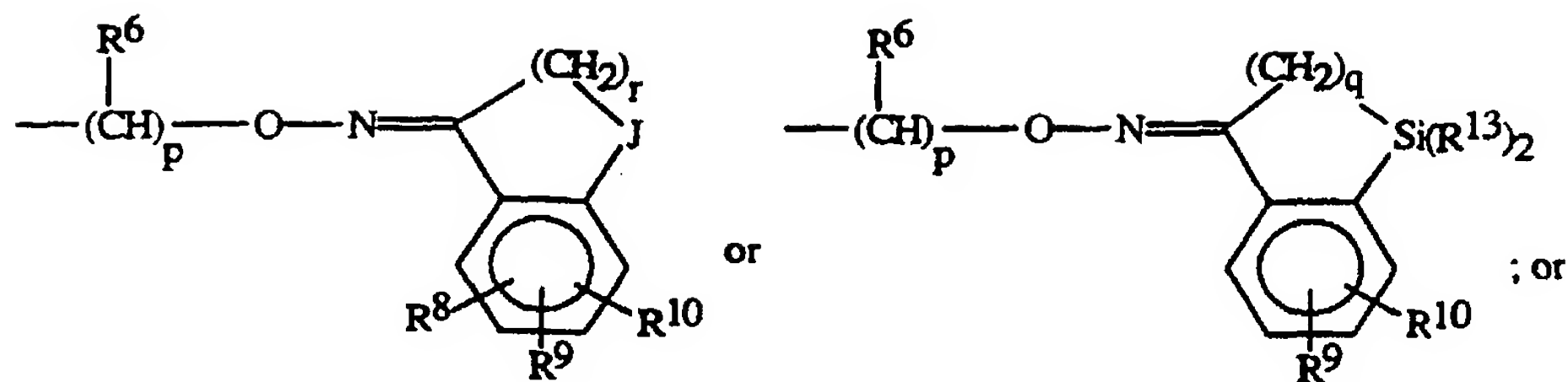


Z-37

each group substituted with R^8 and optionally substituted with one of R^9 , R^{10} , or both R^9 and R^{10} ; or

Y and Z are taken together to form

11



R^3 , Y, and Z are taken together with the phenyl ring to form a naphthalene moiety substituted on either ring with R^8 and with a floating R^4 ;

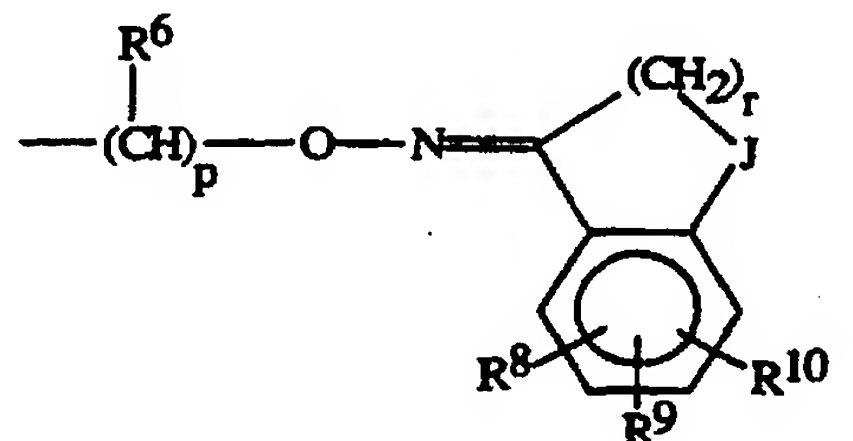
5 R^9 is H; 1-2 halogen; C_1 - C_6 alkyl; C_1 - C_6 haloalkyl; C_1 - C_6 alkoxy; C_1 - C_6 haloalkoxy; C_1 - C_6 alkylthio; C_3 - C_6 cycloalkyl; $CO_2(C_1$ - C_6 alkyl); $NH(C_1$ - C_6 alkyl); $N(C_1$ - C_6 alkyl) $_2$; cyano; $SiR^{22}R^{23}R^{24}$; or $GeR^{22}R^{23}R^{24}$; or R^9 is phenyl, phenoxy, pyridinyl, pyridinyloxy, pyrimidinyl, or pyrimidinyloxy each optionally substituted with R^{11} and R^{12} ; and

10 R^{25} is H; C_1 - C_6 alkyl; C_1 - C_6 haloalkyl; or phenyl optionally substituted with halogen, C_1 - C_4 alkyl, C_1 - C_4 haloalkyl, C_1 - C_4 alkoxy, C_1 - C_4 haloalkoxy, nitro or cyano.

Preferred 2. Compounds of Preferred 1 wherein:

15 Z is phenyl substituted with R^8 , R^9 , and R^{10} ; or Z is Z-1 to Z-21, each substituted with R^8 and optionally substituted with one of R^9 , R^{10} , or both R^9 , and R^{10} ; or

Y and Z are taken together to form



20 J is $-CH_2-$ or $-CH_2CH_2-$;
p is 0; and
r is 1.

Preferred 3. Compounds of Preferred 2 wherein:

25 when E is E^1 , then A is O; N; NR^5 ; or CR^{14} ; and X is OR^1 ;
 R^1 is C_1 - C_3 alkyl;
 R^2 is H or C_1 - C_2 alkyl;
 R^3 and R^4 are each H;

Y is -O-; -CH=CH-; -CH₂O-; -OCH₂-; -CH₂O-N=C(R⁷)-; or
-CH₂OC(=O)NH-;

R⁷ is H; C₁-C₃ alkyl; or C₁-C₃ haloalkyl; and

Z is phenyl substituted with R⁸, R⁹, and R¹⁰; or Z is Z-16, Z-18, or Z-1,
each substituted with R⁸ and optionally substituted with one of R⁹,
R¹⁰ or both R⁹ and R¹⁰.

Preferred 4. Compounds of Preferred 3 wherein:

E is E¹;

A is O or NR⁵;

G is C;

Y is -O-; -CH₂O-; -OCH₂-; or -CH₂O-N=C(R⁷)-; and

R⁷ is H; C₁-C₂ alkyl; or C₁-C₂ haloalkyl.

Preferred 5. Compounds of Preferred 3 wherein:

E is E¹;

A is N or CR¹⁴;

G is N;

Y is -O-; -CH₂O-; -OCH₂-; or -CH₂O-N=C(R⁷)-;

R⁷ is H; C₁-C₂ alkyl; or C₁-C₂ haloalkyl.

Preferred 6. Compounds of Preferred 2 wherein:

E is E², E³, E⁴, E⁵, or E⁶.

Preferred 7. Compounds of Preferreds 2 through 6 wherein:

R¹ is methyl;

R² is methyl; and

Z is phenyl substituted with R⁸, R⁹, and R¹⁰.

Most preferred are compounds of Preferred 3 selected from the group:

2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-(trimethylsilyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3H-1,2,4-triazol-3-one;

methyl α-(methoxyimino)-2-[[2-methyl-4-

(trimethylgermyl)phenoxy]methyl]benzeneacetate;

methyl 2-[[[1-[3-(dimethylphenylsilyl)phenyl]ethylidene]amino]oxy]methyl]-α-(methoxyimino)benzeneacetate;

methyl α-(methoxyimino)-2-[[[1-[3-

(trimethylgermyl)phenyl]ethylidene]amino]oxy]methyl]benzeneacetate; and

methyl α-(methoxyimino)-2-[[[1-[3-

(trimethylsilyl)phenyl]ethylidene]amino]oxy]methyl]benzeneacetate.

This invention also relates to fungicidal compositions comprising fungicidally effective amounts of the compounds of Formula I and at least one of a surfactant, a solid

diluent or a liquid diluent. The preferred compositions of the present invention are those which comprise the above preferred compounds.

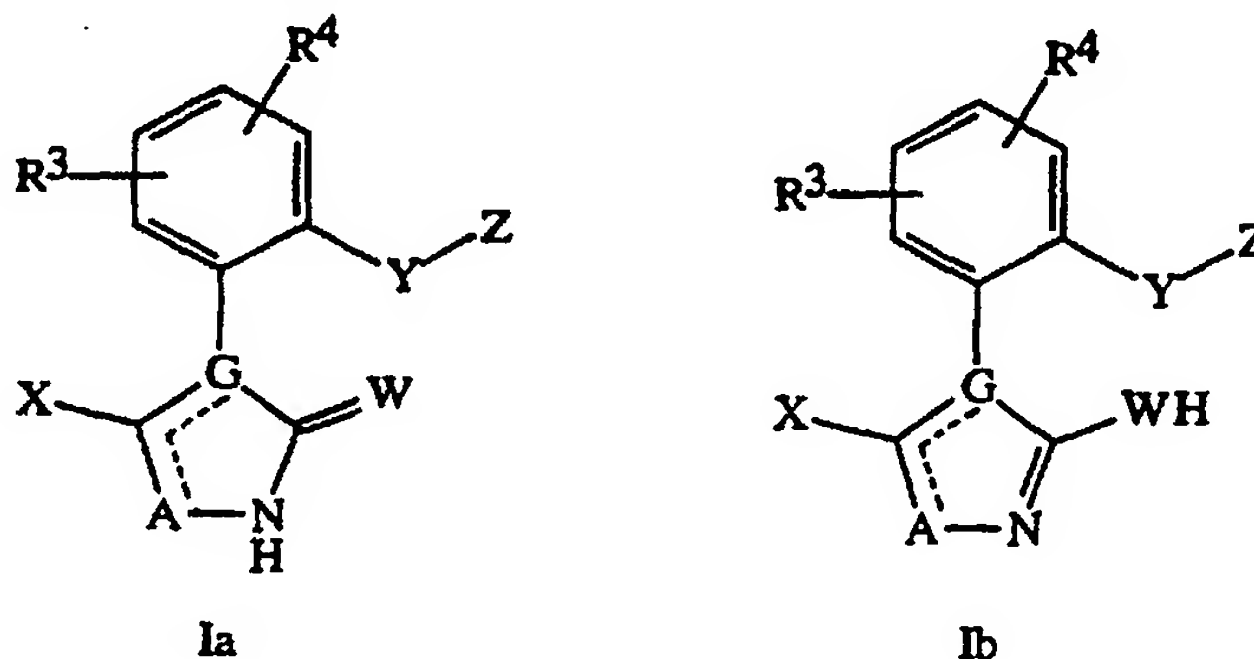
This invention also relates to a method for controlling plant diseases caused by fungal plant pathogens comprising applying to the plant or portion thereof, or to the
5 plant seed or seedling, a fungicidally effective amount of the compounds of Formula I (e.g., as a composition described herein). The preferred methods of use are those involving the above preferred compounds.

This invention also relates to arthropodicidal compositions comprising arthropodically effective amounts of the compounds of Formula I and at least one of a
10 surfactant, a solid diluent or a liquid diluent. The preferred compositions of the present invention are those which comprise the above preferred compounds.

This invention also relates to a method for controlling arthropods comprising contacting the arthropods or their environment with an arthropodically effective amount of the compounds of Formula I (e.g., as a composition described herein). The
15 preferred methods of use are those involving the above preferred compounds.

The compounds of Formula I can be prepared by one or more of the following methods and variations as described in Schemes 1-30. The definitions of E, A, G, W, X, Y, Z, J, R¹-R²⁴, m, n, p, r, s and q in the compounds of Formulae 1-44d below are as defined above in the Summary of the Invention. Compounds of Formulae Ia-Is are
20 various subsets of the compounds of Formula I where E = E¹, and all substituents for Formulae Ia-Is are as defined above for Formula I.

One skilled in the art will recognize that some compounds of Formula I can exist in one or more tautomeric forms. For example, a compound of Formula I wherein E is E¹ and R² is H may exist as tautomer Ia or Ib, or both Ia and Ib. The present invention
25 comprises all tautomeric forms of compounds of Formula I where E = E¹.



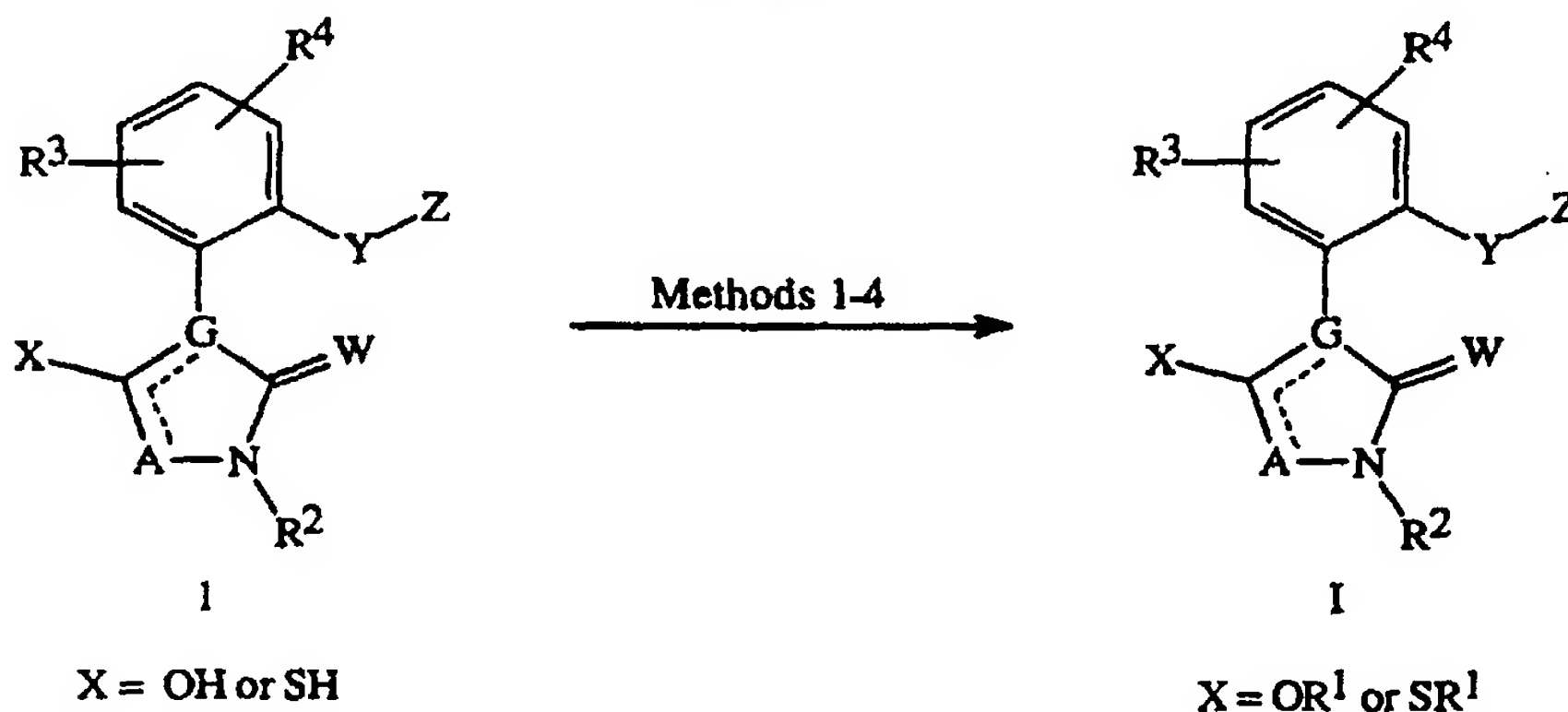
The compounds of Formula I where E = E¹ can be prepared as described below in Procedures 1) to 5). Procedures 1) to 4) describe syntheses involving construction of

the heterocycle after the formation of the aryl moiety. Procedure 5) describes syntheses of the aryl moiety with the E-moiety amide ring already in place.

1) Alkylation Procedures

The compounds of Formula I where $E = E^1$ are prepared by treating compounds of Formula 1 with an appropriate alkyl transfer reagent in an inert solvent with or without additional acidic or basic reagents or other reagents (Scheme 1). Suitable solvents are selected from the group consisting of polar aprotic solvents such as acetonitrile, dimethylformamide or dimethyl sulfoxide; ethers such as tetrahydrofuran, dimethoxyethane, or diethyl ether; ketones such as acetone or 2-butanone; hydrocarbons such as toluene or benzene; and halocarbons such as dichloromethane or chloroform.

Scheme 1



Method 1: $U-CH=N_2$ ($U = H \text{ or } (CH_3)_3Si$)
2

Method 2: $Cl_3C-C(=O)NH-OR^1$; Lewis acid
3

Method 3: $(R^1)_3O^+ BF_4^-$
4

Method 4: $(R^1)_2SO_4$; R^1OSO_2Q ; or R^1-hal ;
optional base
($hal = F, Cl, Br, \text{ or } I$)
($Q = C_1-C_6 \text{ alkyl, } C_1-C_6 \text{ haloalkyl}$)

For example, compounds of Formula I where $E = E^1$ can be prepared by the action of diazoalkane reagents of Formula 2 such as diazomethane ($U = H$) or trimethylsilyldiazomethane ($U = (CH_3)_3Si$) on compounds of Formula 1 (Method 1).

Use of trimethylsilyldiazomethane requires a protic cosolvent such as methanol. For examples of these procedures, see *Chem. Pharm. Bull.*, (1984), 32, 3759.

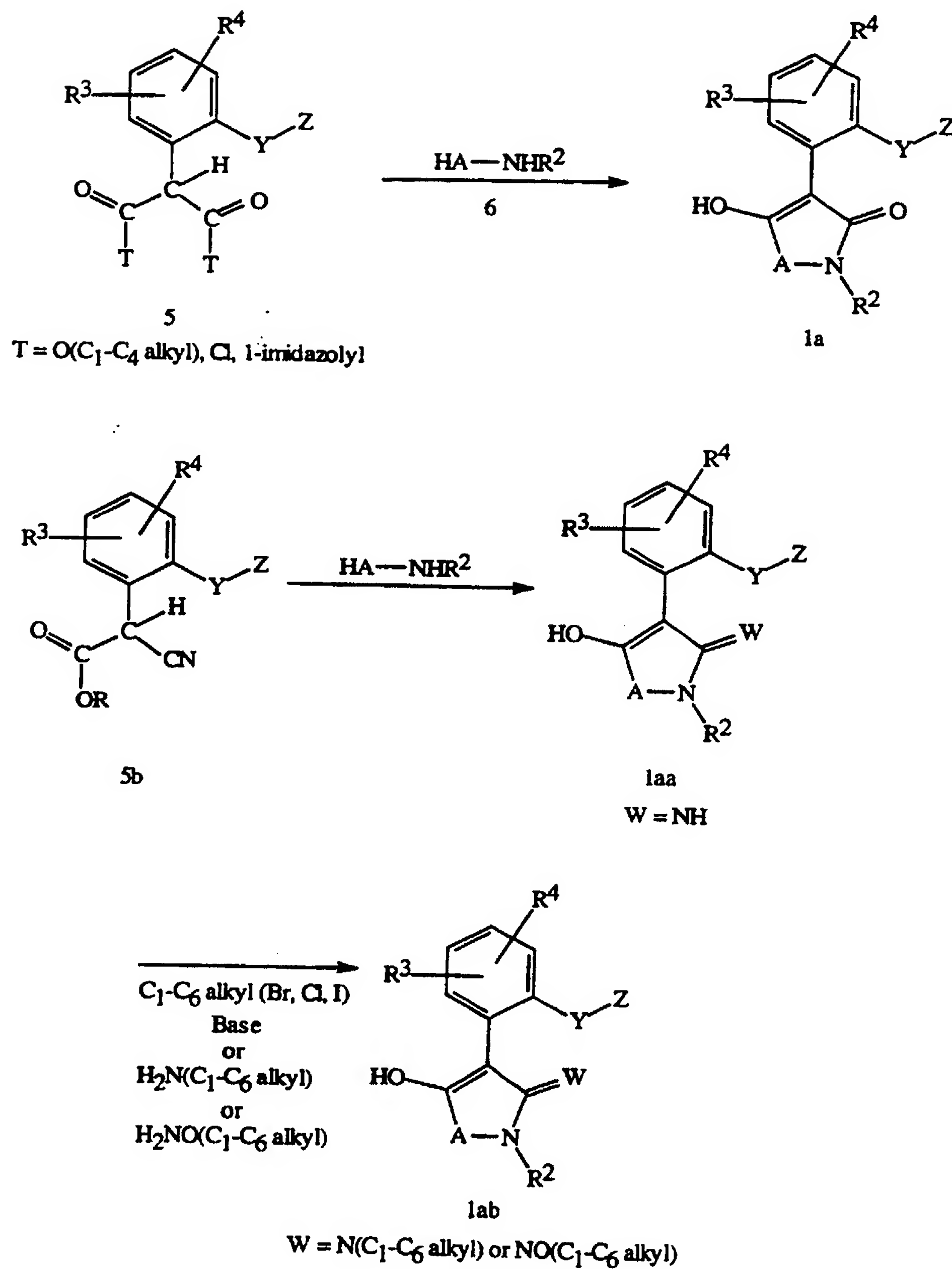
As indicated in Method 2, compounds of Formula I where $E = E^1$ can also be prepared by contacting carbonyl compounds of Formula 1 with alkyl
5 trichloroacetimidates of Formula 3 and a Lewis acid catalyst. Suitable Lewis acids include trimethylsilyl triflate and tetrafluoroboric acid. The alkyl trichloroacetimidates can be prepared from the appropriate alcohol and trichloroacetonitrile as described in the literature (J. Danklmaier and H. Hönig, *Synth. Commun.*, (1990), 20, 203).

Compounds of Formula I where $E = E^1$ can also be prepared from compounds of
10 Formula 1 by treatment with a trialkyloxonium tetrafluoroborate (e.g., Meerwein's salt) of Formula 4 (Method 3). The use of trialkyloxonium salts as powerful alkylating agents is well known in the art (see U. Schöllkopf, U. Groth, C. Deng, *Angew. Chem., Int. Ed. Engl.*, (1981), 20, 798).

Other alkylating agents which can convert carbonyl compounds of Formula 1 to
15 compounds of Formula I where $E = E^1$ are dialkyl sulfates such as dimethyl sulfate, haloalkyl sulfonates such as methyl trifluoromethanesulfonate, and alkyl halides such as iodomethane and propargyl bromide (Method 4). These alkylations can be conducted with or without additional base. Appropriate bases include alkali metal alkoxides such as potassium *tert*-butoxide, inorganic bases such as sodium hydride and potassium
20 carbonate, pyridine, or tertiary amines such as triethylamine, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and triethylenediamine. See R. E. Benson, T. L. Cairns, *J. Am. Chem. Soc.*, (1948), 70, 2115 for alkylation examples using agents of this type.

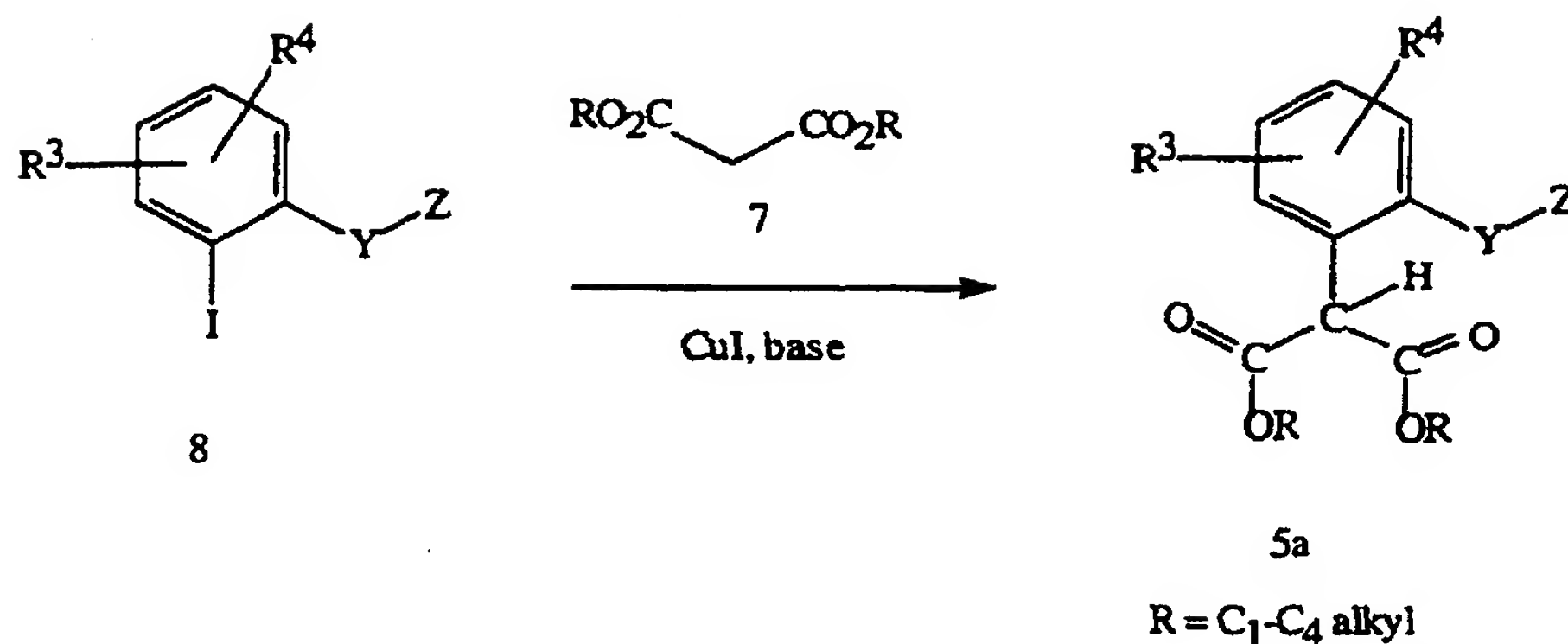
Compounds of Formula 1a (compounds of Formula 1 wherein $G = C$, $W = O$ and
25 $X = OH$) can be prepared by condensation of malonates or malonate derivatives of Formula 5 with an ambident nucleophile of Formula 6 (Scheme 2). The nucleophiles of Formula 6 are *N*-substituted hydroxylamines ($HO-NHR^2$) and substituted hydrazines ($HN(R^5)-NHR^2$). Examples of such nucleophiles are *N*-methylhydroxylamine and methylhydrazine. The preparation of the malonate esters of Formula 5 can be prepared
30 by methods described hereinafter. The esters of Formula 5 can also be activated by first hydrolyzing the ester to form the corresponding carboxylic acid, and then converting the acid into the acid chloride ($T = Cl$) using thionyl chloride or oxalyl chloride, or into the acyl imidazole ($T = 1$ -imidazolyl) by treating with 1,1'-carbonyldiimidazole. Compounds of Formula 1aa can be prepared by reaction of nitrile esters of Formula 5b with ambident
35 nucleophiles of Formula 6. See M. Scobie and G. Tennant, *J. Chem. Soc., Chem. Comm.*, (1994), 2451. Alkylation of 1aa with alkyl halides in the presence of base provides compounds of Formula 1ab. Alternatively, treatment of 1aa with alkylamines or alkoxyamines provides compounds of Formula 1ab.

Scheme 2

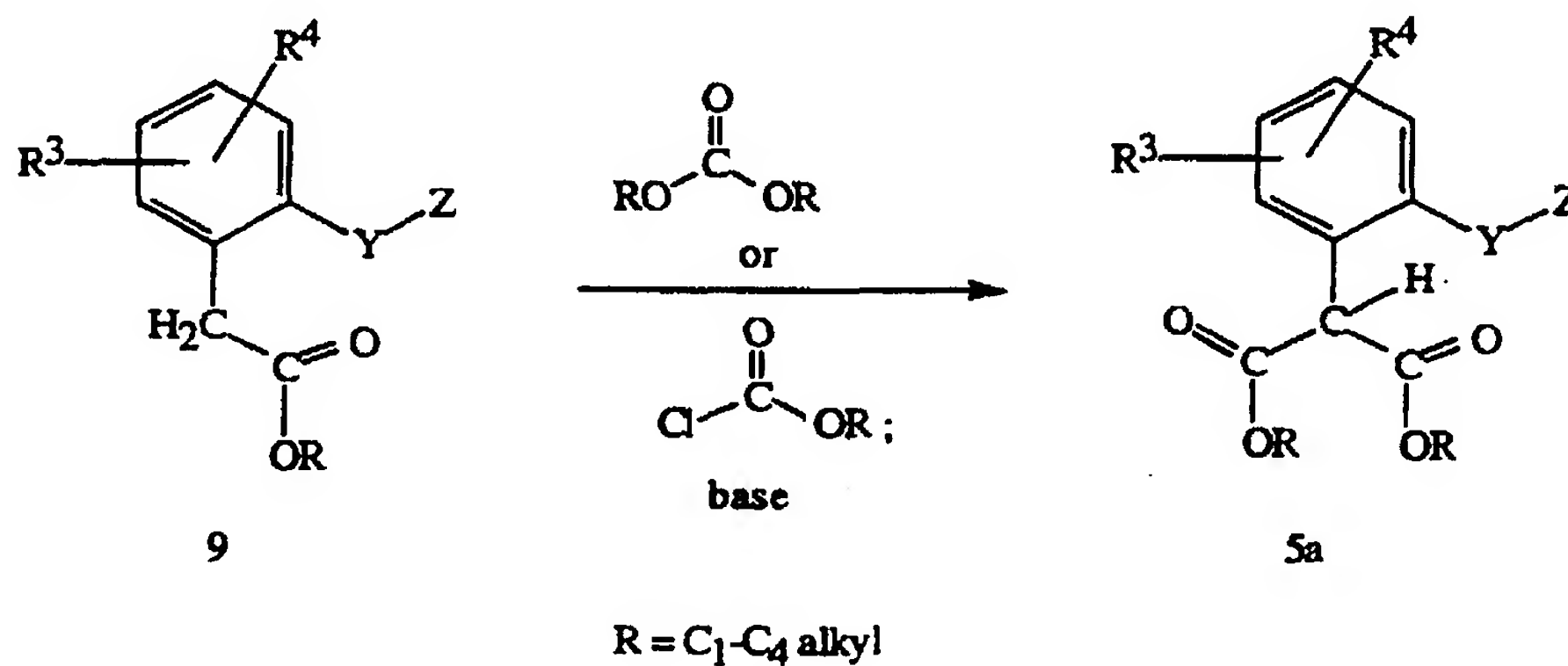


Esters of Formula 5a can be prepared from copper (I)-catalyzed reaction of malonate esters of Formula 7 with substituted iodobenzenes of Formula 8 according to methods adapted from A. Osuka, T. Kobayashi and H. Suzuki, *Synthesis*, (1983), 67, and illustrated in Scheme 3.

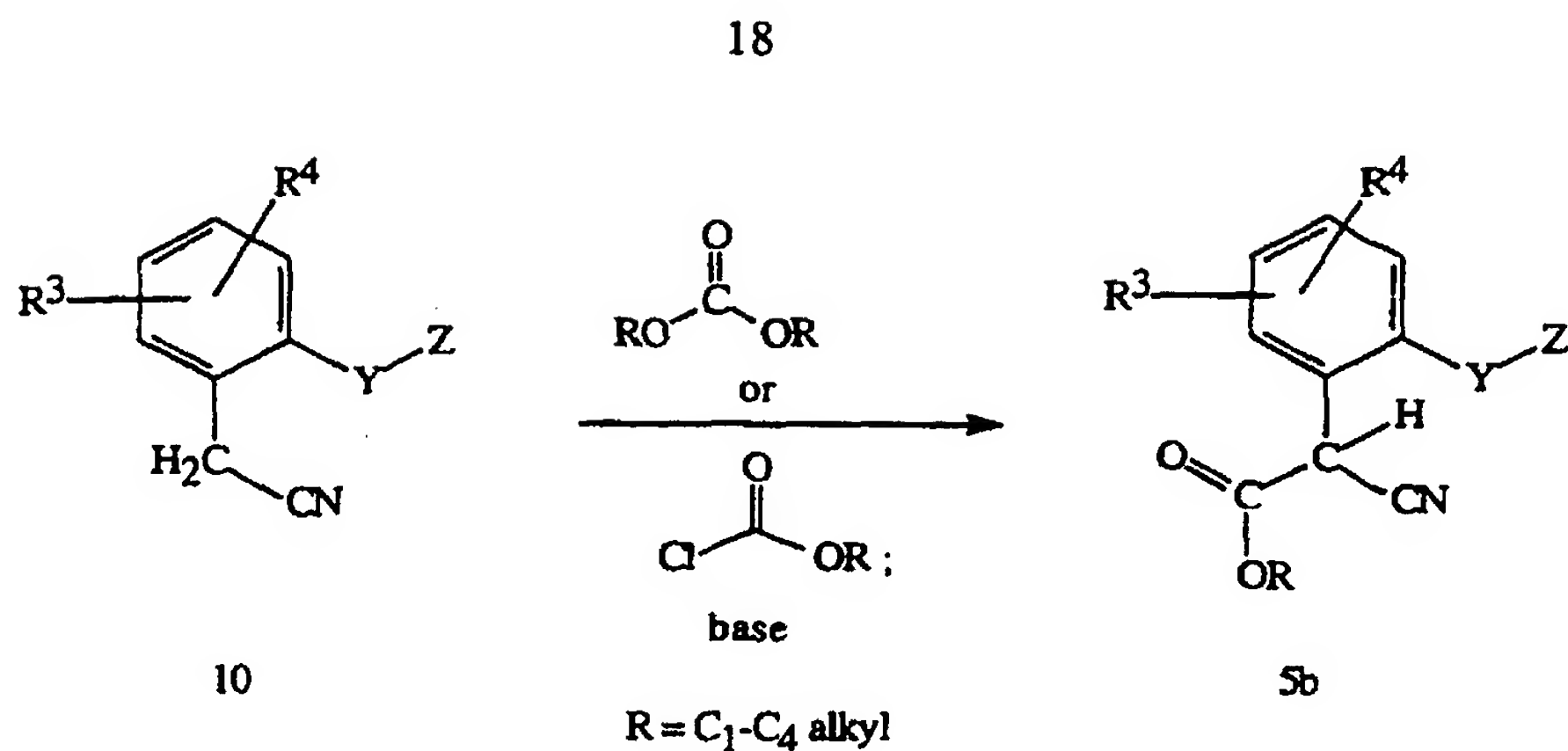
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Scheme 3

- 5 Additionally, the malonate esters of Formula 5a can be prepared by treating phenyl acetic acid esters of Formula 9 with a dialkyl carbonate or alkyl chloroformate in the presence of a suitable base such as, but not limited to, sodium metal and sodium hydride (Scheme 4). For example, see *J. Am. Chem. Soc.*, (1928), 50, 2758. Nitrile esters of Formula 5b can be prepared similarly from compounds of Formula 10.

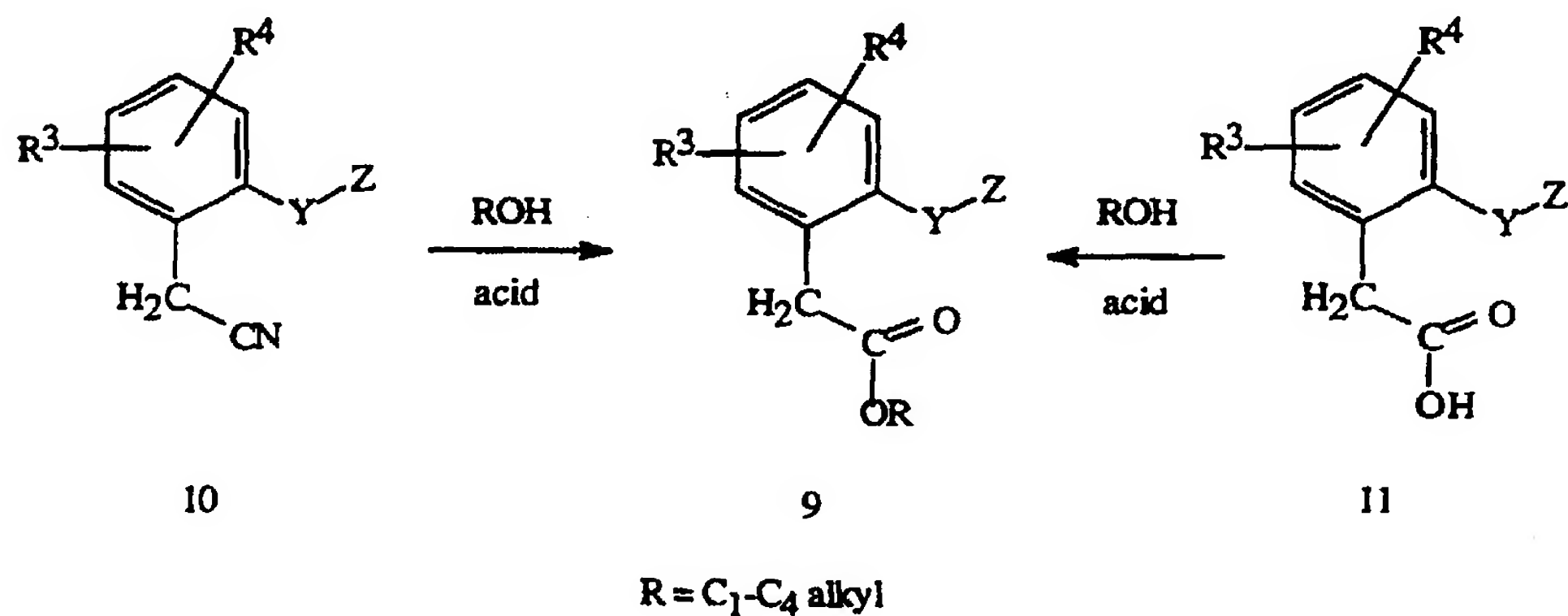
Scheme 4

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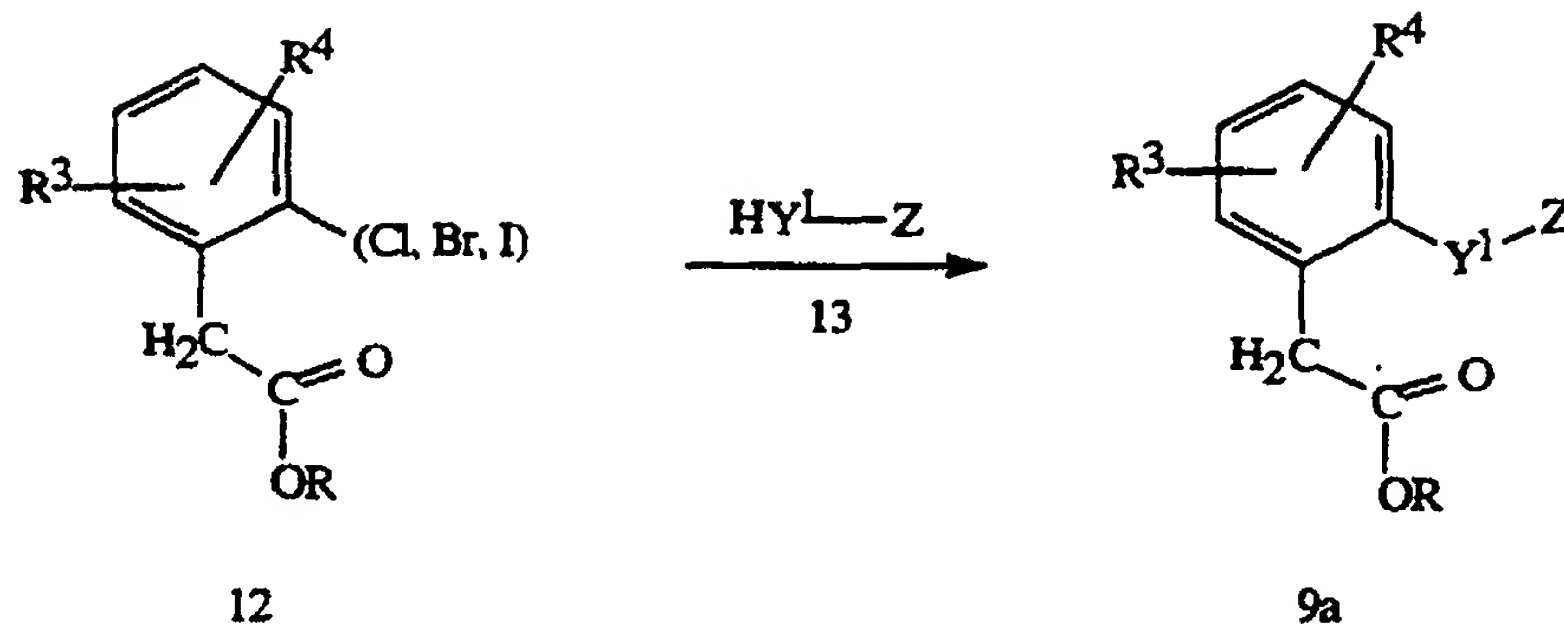
Esters of Formula 9 can be prepared from acid-catalyzed alcoholysis of phenyl acetonitriles of Formula 10 or by esterification of phenyl acetic acids of Formula 11 as illustrated in Scheme 5 (see *Org. Synth., Coll. Vol. I*, (1941), 270).

Scheme 5

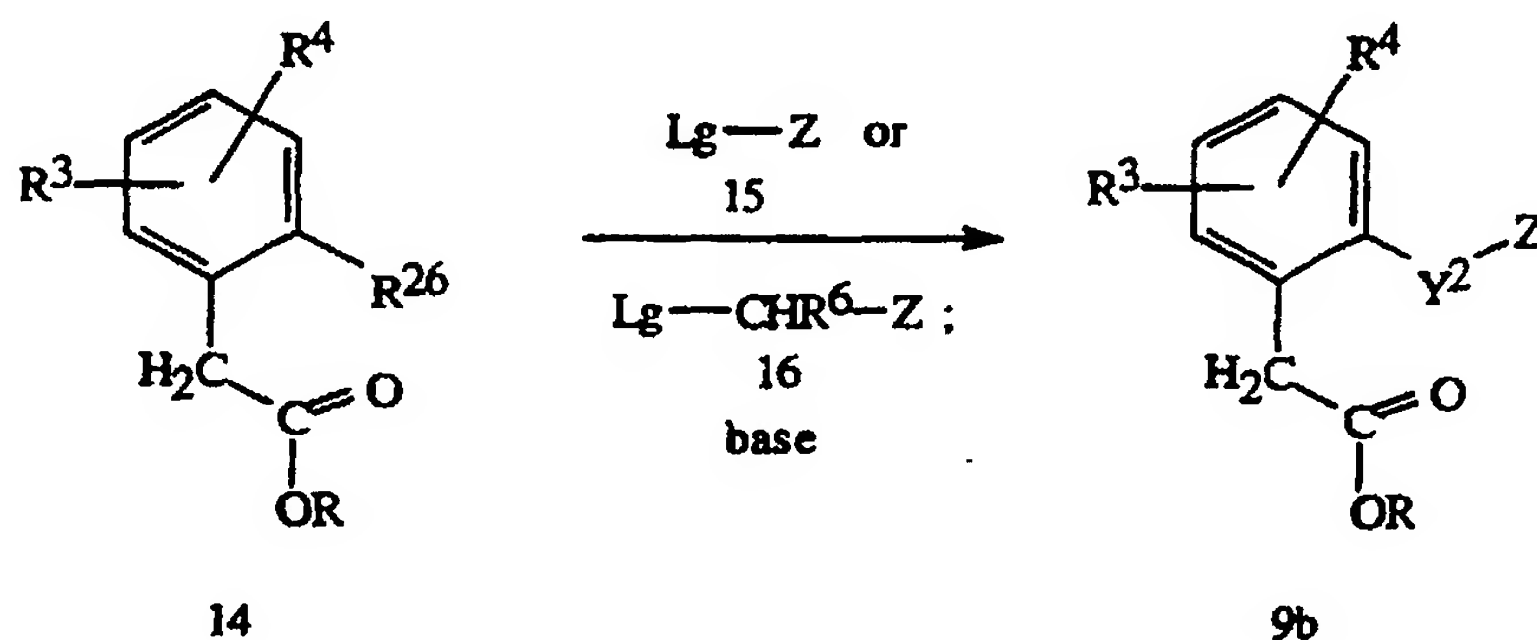


Phenyl acetic acid esters of Formula 9a can also be prepared by
10 copper (I)-catalyzed condensation of phenyl halides of Formula 12 with compounds of
Formula 13 as described in EP-A-307,103 and illustrated below in Scheme 6.

19

Scheme 6R = C₁-C₄ alkylY¹ = O, S, NR⁶, OCHR⁶, SCHR⁶, O-N=C(R⁷)

Some esters of Formula 9 (Formula 9b) can also be prepared by forming the Y² bridge using conventional nucleophilic substitution chemistry (Scheme 7). Displacement of an appropriate leaving group (Lg) in electrophiles of Formula 15 or 16 with a nucleophilic ester of Formula 14 affords compounds of Formula 9b. A base, for example sodium hydride, is used to generate the corresponding alkoxide or thioalkoxide of the compound of Formula 14.

Scheme 7R = C₁-C₄ alkylR²⁶ = OH, SH, NHR⁶, CHR⁶OH, CHR⁶SHY² = O, S, OCHR⁶, SCHR⁶, CHR⁶O, CHR⁶SLg = Br, Cl, I, OSO₂CH₃, OSO₂(4-Me-Ph)

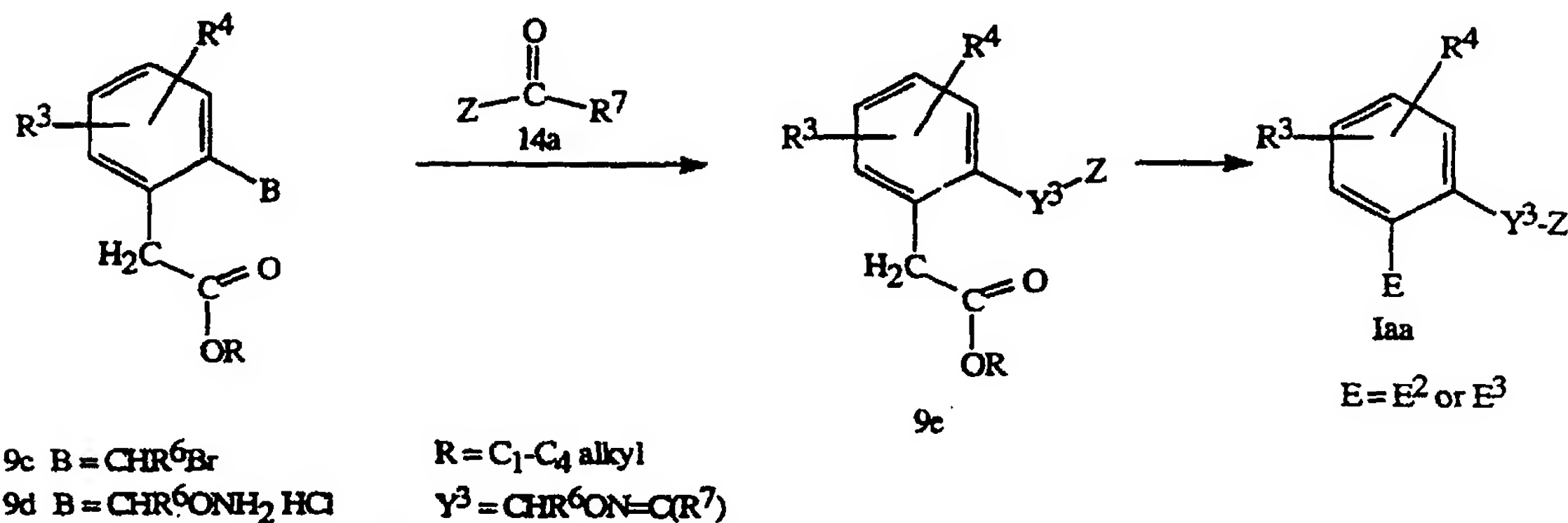
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Some esters of Formula 9 (Formula 9e) can also be prepared by forming the Y³ bridge from substituted hydroxylamine 9d and carbonyl compounds 14a. The hydroxylamine 9d is in turn prepared from esters 9c. This method has been described in EP-A-600,835 and is illustrated in Scheme 8. Esters of Formula 9e can be used to

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prepare compounds of Formula Iaa wherein $E = E^2$ or E^3 by methods described in EP-A-600,835.

Scheme 8



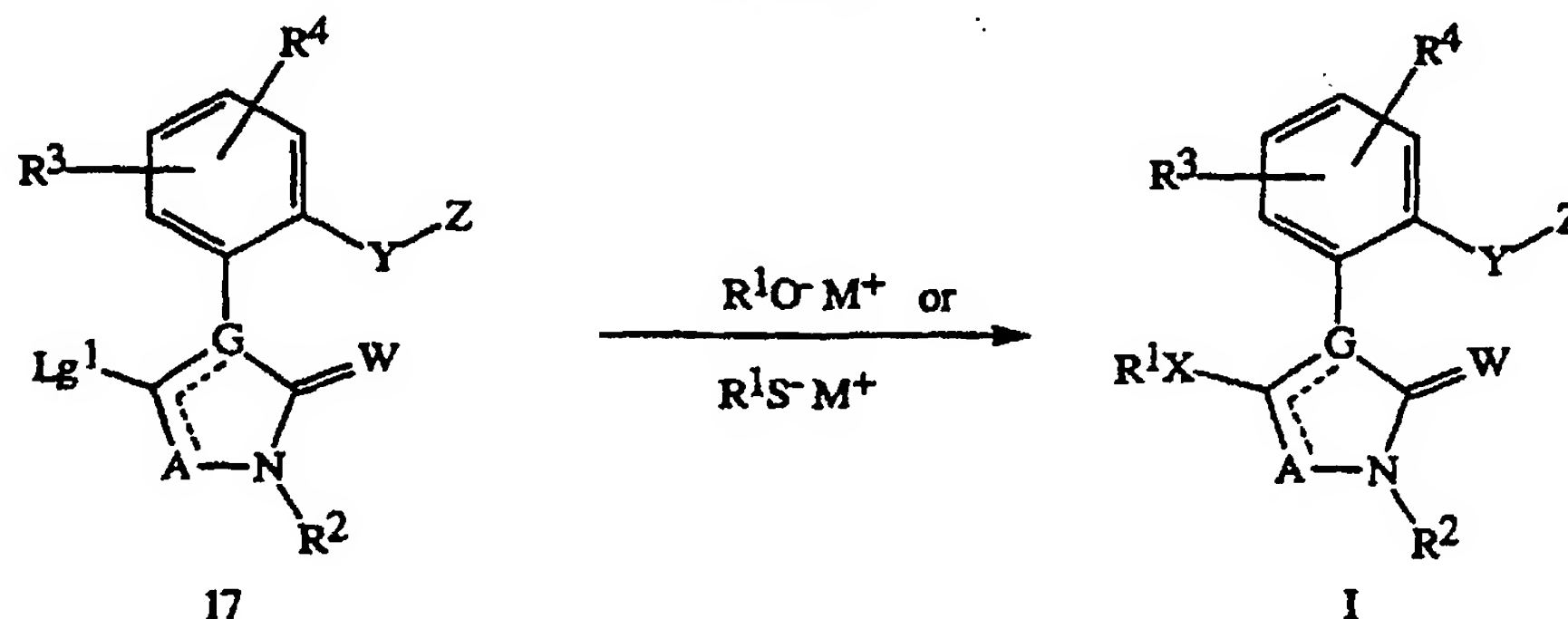
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2) Displacement and Conjugate Addition/Elimination Procedures

Compounds of Formula I where $E = E^1$ can also be prepared by reaction of Formula 17 compounds with alkali metal alkoxides ($\text{R}^1\text{O}^-\text{M}^+$) or alkali metal thioalkoxides ($\text{R}^1\text{S}^-\text{M}^+$) in a suitable solvent (Scheme 9). The leaving group Lg^1 in the amides of Formula 17 is any group known in the art to undergo a displacement reaction of this type. Examples of suitable leaving groups include chlorine, bromine, and sulfonyl and sulfonate groups. Examples of suitable inert solvents are dimethylformamide or dimethyl sulfoxide.

10

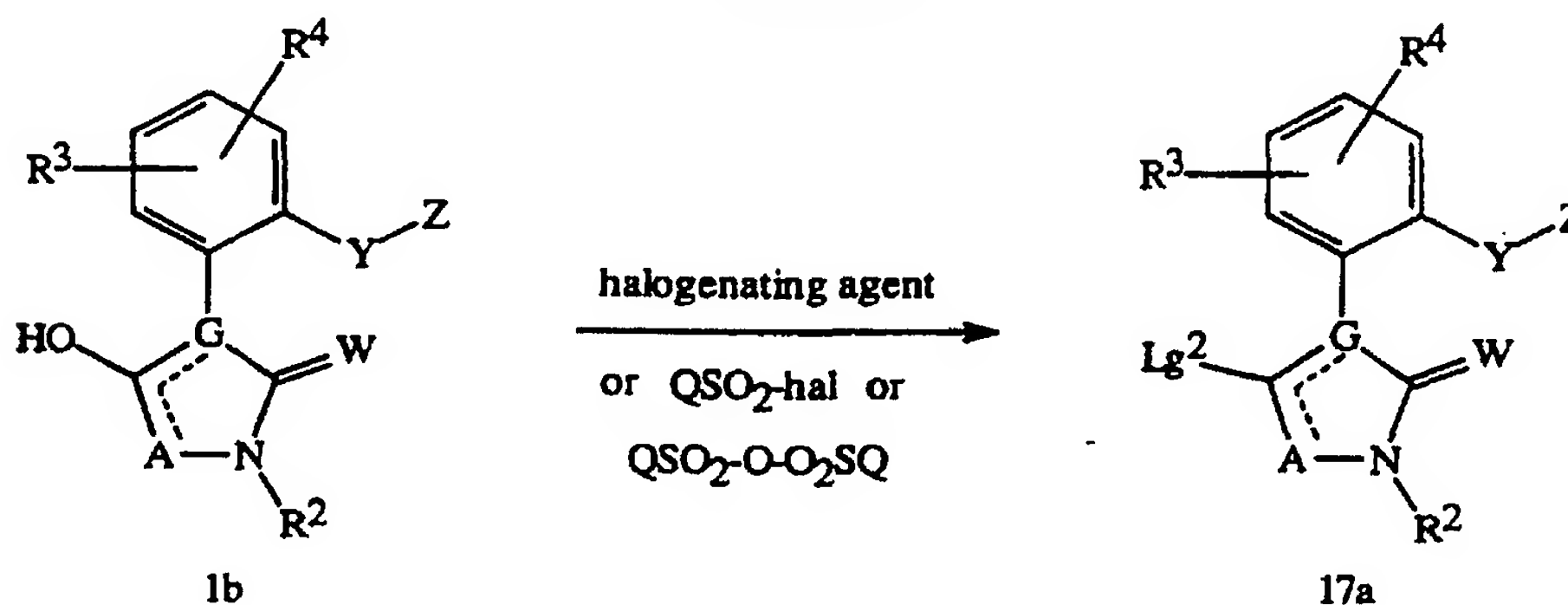
Scheme 9



$\text{Lg}^1 = \text{Cl}, \text{Br}, -\text{SO}_2\text{Q}, \text{ or } -\text{OSO}_2\text{Q}$
 $\text{Q} = \text{C}_1\text{-C}_6 \text{ alkyl or } \text{C}_1\text{-C}_6 \text{ haloalkyl}$
 $\text{M} = \text{K or Na}$

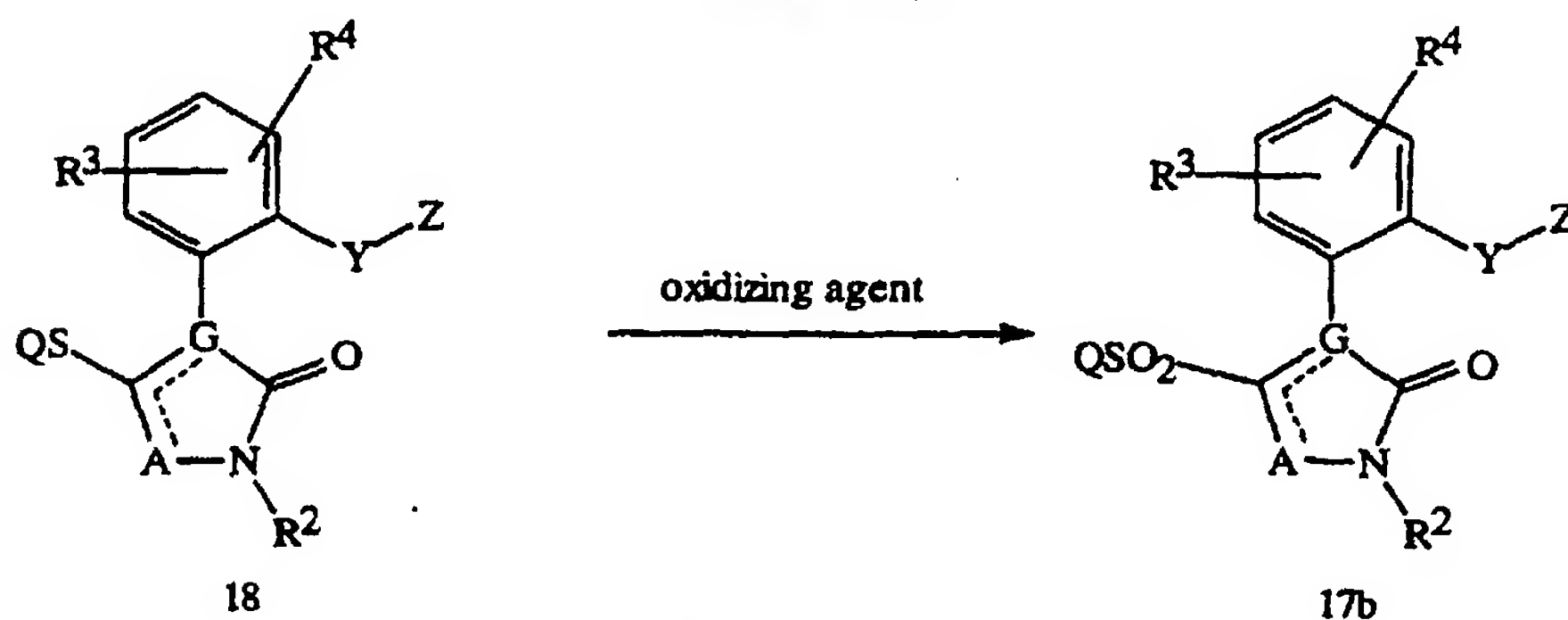
Compounds of Formula 17a can be prepared from compounds of Formula 1b (compounds of Formula 1 wherein X is OH) by reaction with halogenating agents such as thionyl chloride or phosphorus oxybromide to form the corresponding β -halo-substituted derivatives (Scheme 10). Alternatively, compounds of Formula 1b can be treated with an alkylsulfonyl halide or haloalkylsulfonyl anhydride, such as methane sulfonyl chloride, *p*-toluenesulfonyl chloride, and trifluoromethanesulfonyl anhydride, to form the corresponding β -alkylsulfonate of Formula 17a. The reaction with the sulfonyl halides may be performed in the presence of a suitable base (e.g., triethylamine).

Scheme 10



As illustrated in Scheme 11, sulfonyl compounds of Formula 17b can be prepared by oxidation of the corresponding thio compound of Formula 18 using well-known methods for the oxidation of sulfur (see Schrenk, K. in *The Chemistry of Sulphones and Sulphoxides*; Patai, S. et al., Eds.; Wiley: New York, 1988). Suitable oxidizing reagents include *meta*-chloro-peroxybenzoic acid, hydrogen peroxide and Oxone[®] (KHSO₅).

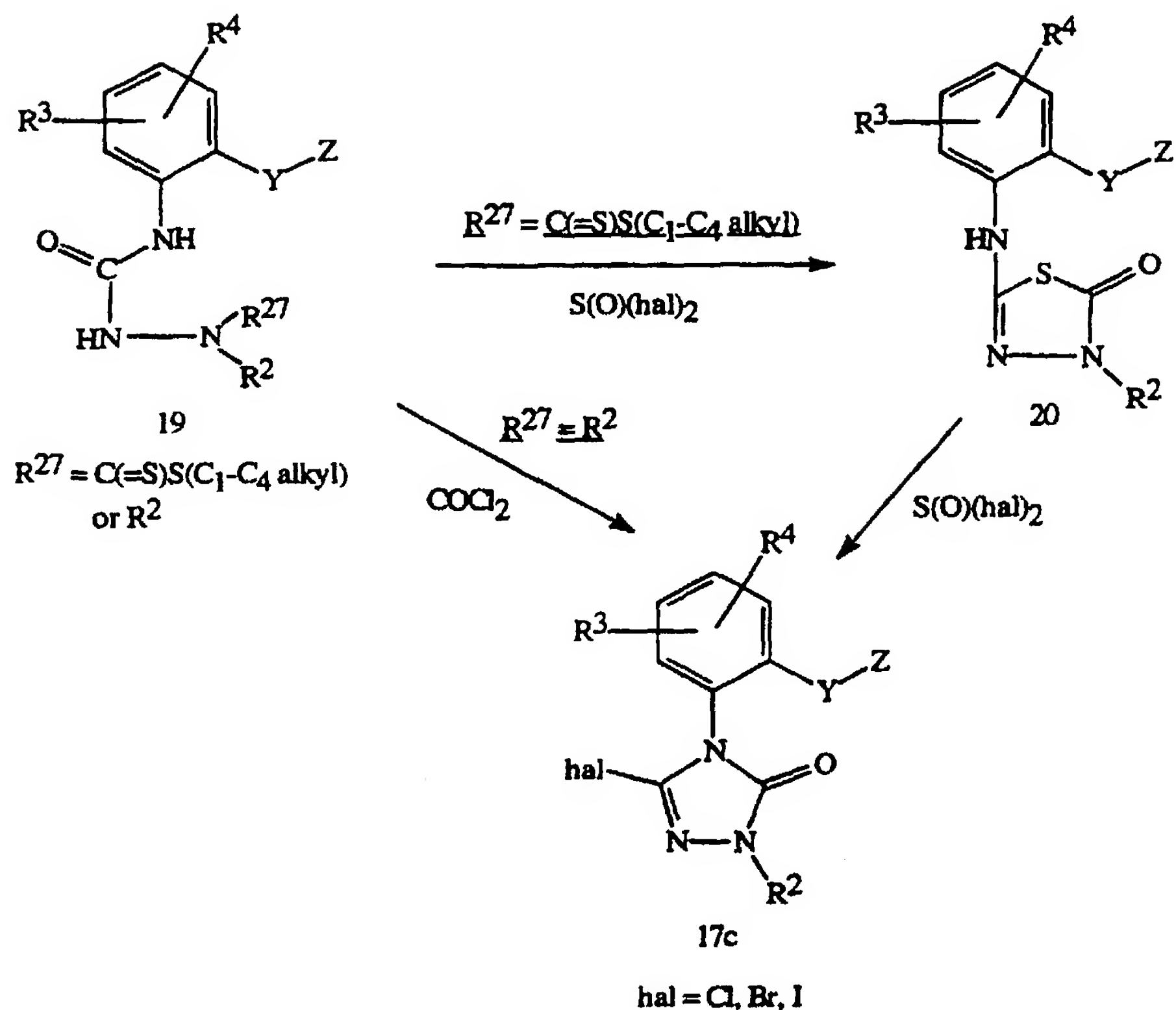
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Scheme 11Q = C₁-C₆ alkyl or C₁-C₆ haloalkyl

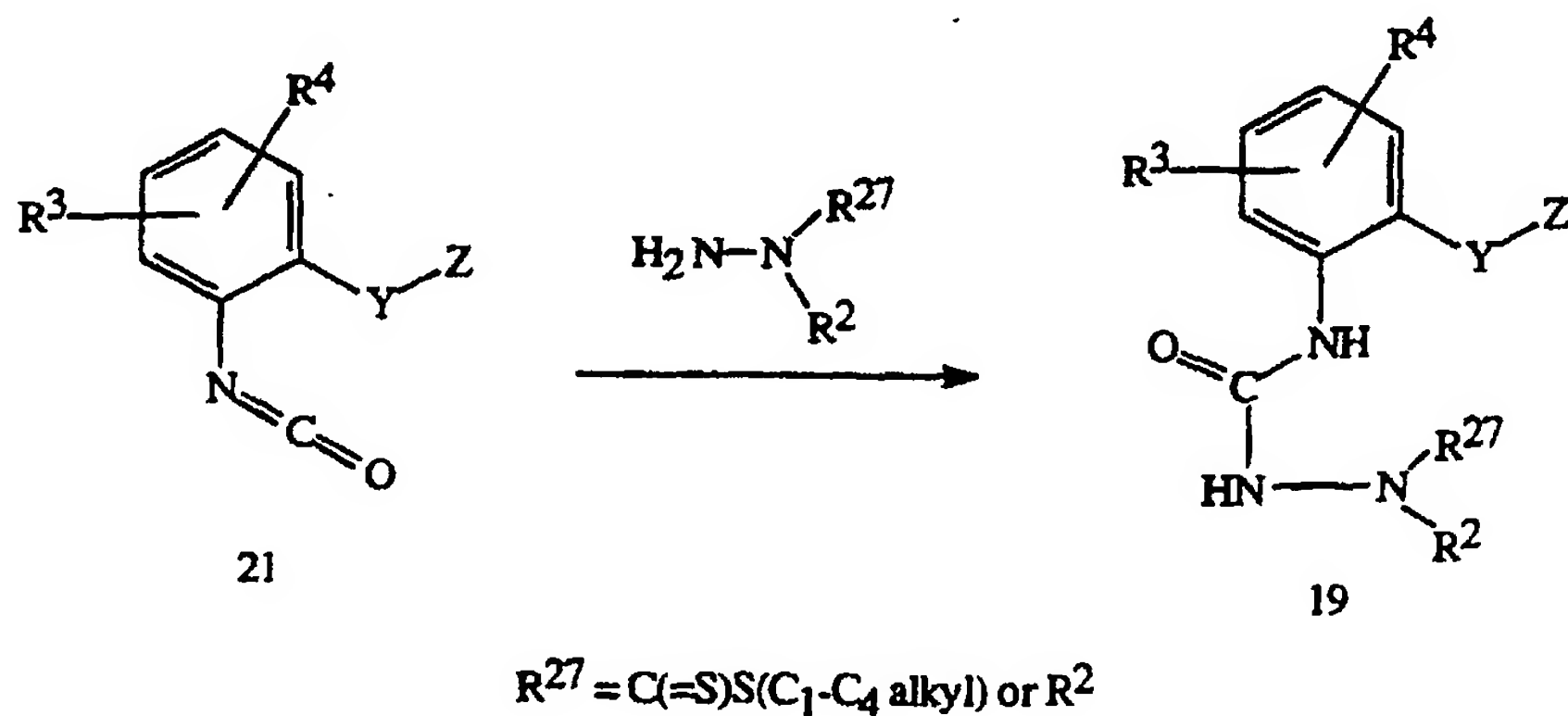
Alternatively, halo-compounds of Formula 17c (compounds of Formula 17a wherein A = N, G = N, and W = O) can be prepared from hydrazides of Formula 19 as illustrated in Scheme 12. When R²⁷ = C(=S)S(C₁-C₄ alkyl), the diacyl compound of Formula 19 is treated with excess of a thionyl halide such as thionyl chloride. The product formed first is the ring-closed compound of Formula 20 which can be isolated or converted *in situ* to the compound of Formula 17c; see P. Molina, A. Tárraga, A. Espinosa, *Synthesis*, (1989), 923 for a description of this process.

Alternatively, when R²⁷ = R² as defined above, the hydrazide of Formula 19 is cyclized with phosgene to form the cyclic urea of Formula 17c wherein hal = Cl. This procedure is described in detail in *J. Org. Chem.*, (1989), 54, 1048.

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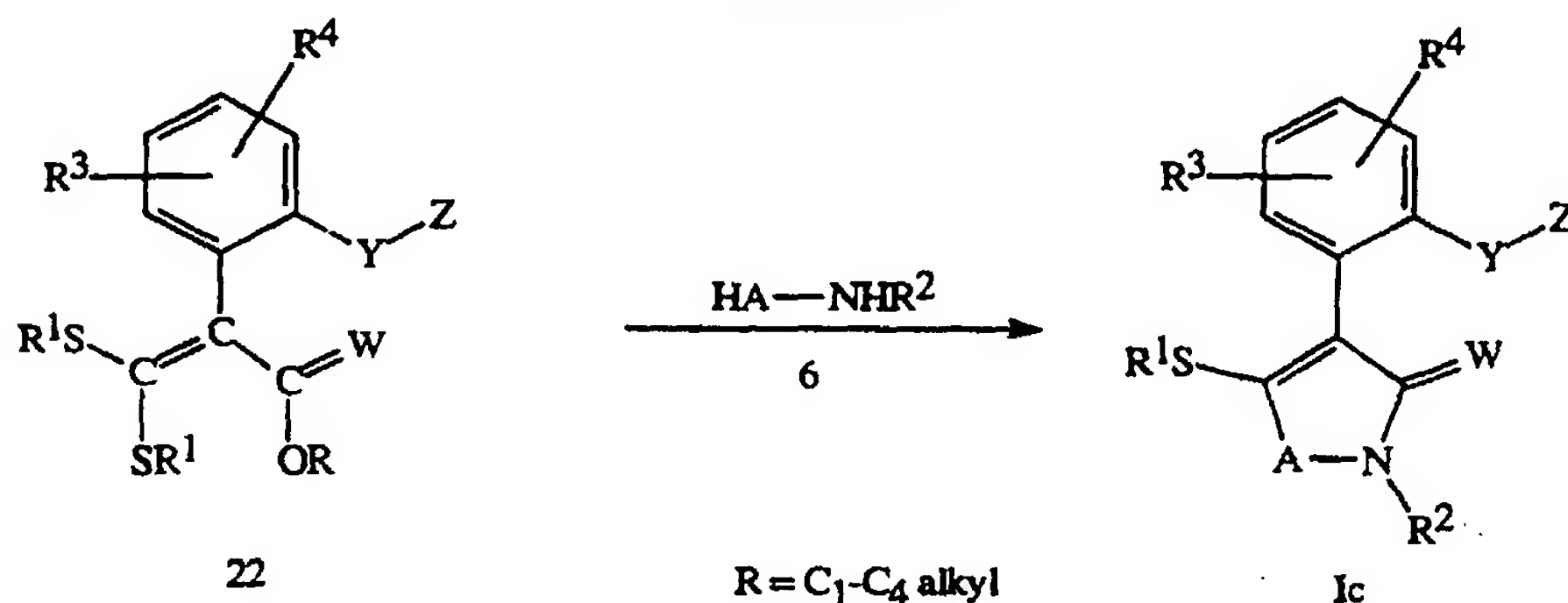
Scheme 12

The hydrazides of Formula 19 can be prepared as illustrated in Scheme 13. Condensation of the isocyanate of Formula 21 with the hydrazine of Formula 5 $H_2NNR^2R^{27}$ in an inert solvent such as tetrahydrofuran affords the hydrazide.

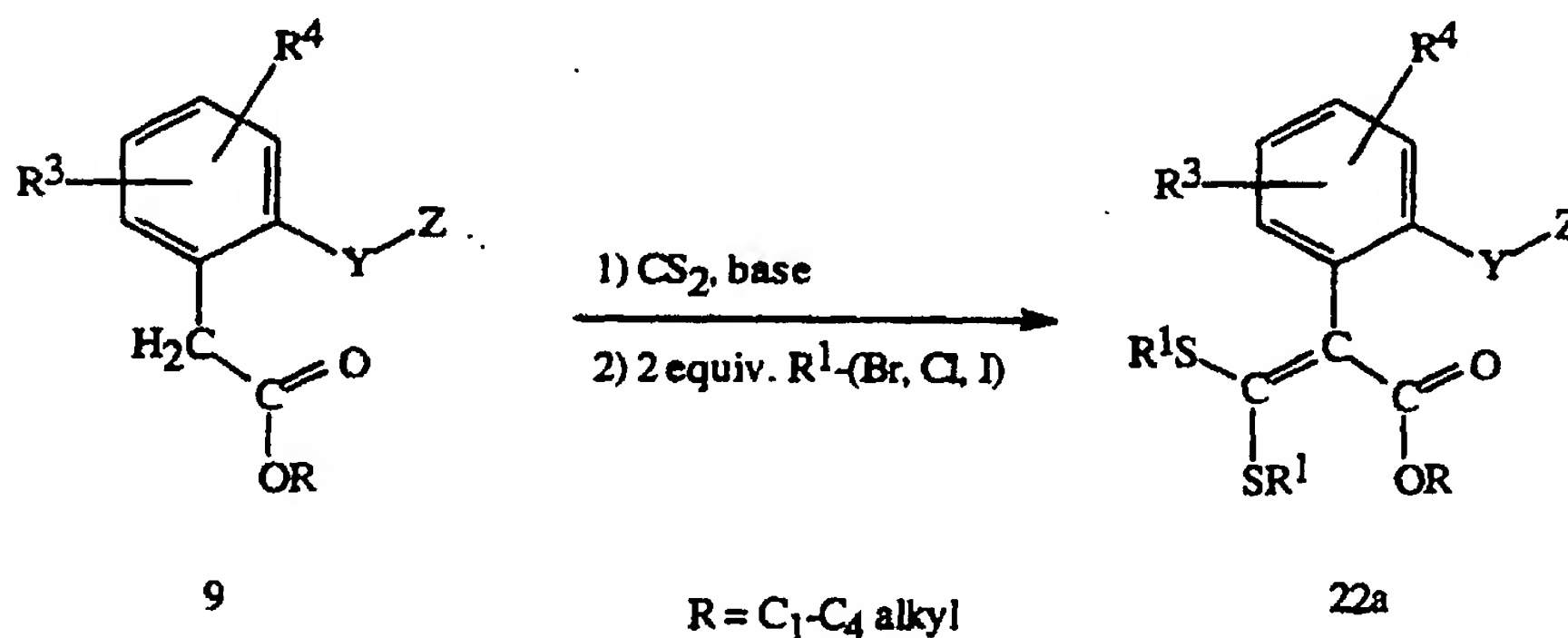
Scheme 13

3) Conjugate Addition/Cyclization Procedures

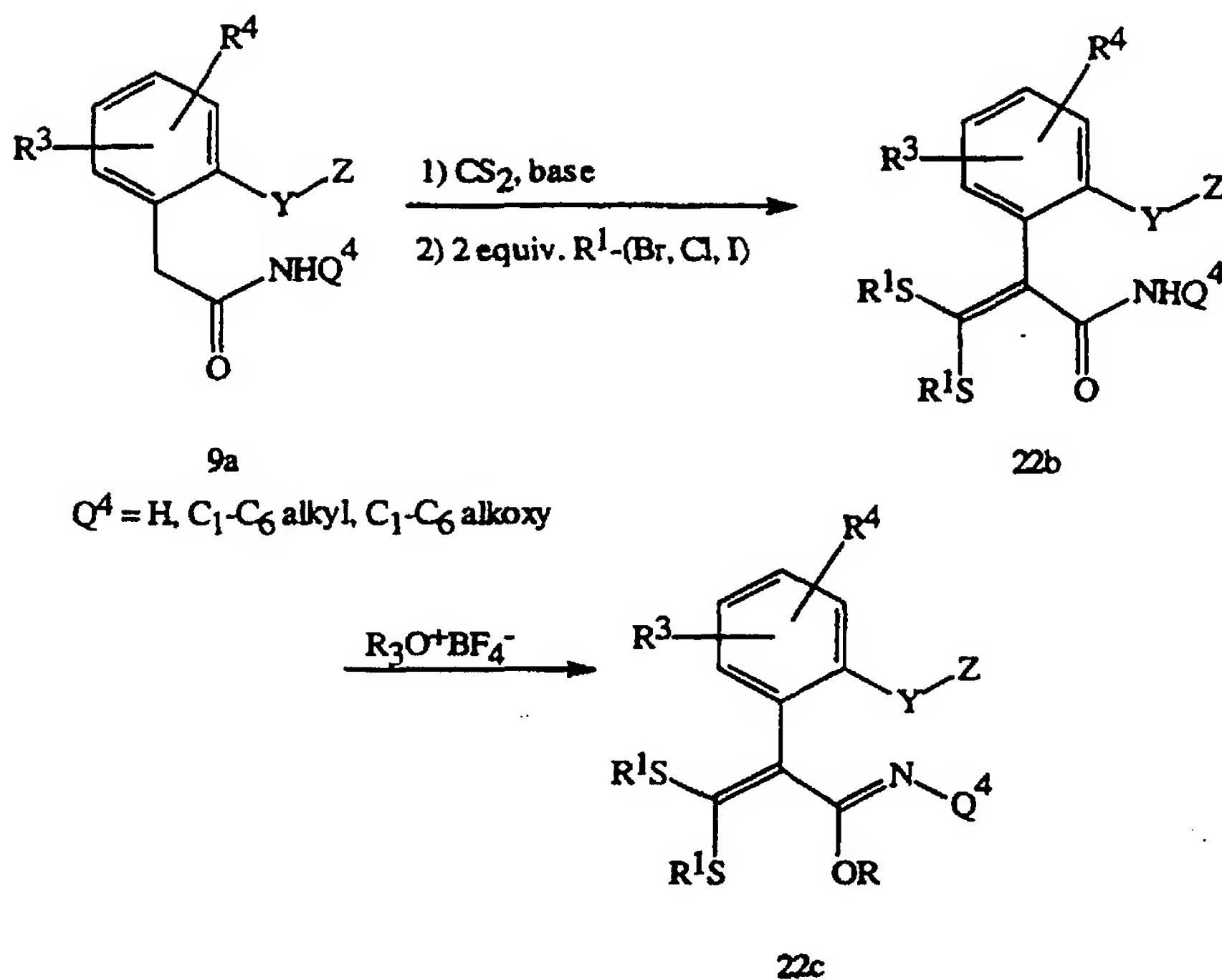
In addition to the methods disclosed above, compounds of Formula I wherein $X = SR^1$ and $G = C$ (Formula Ic) can be prepared by treating a ketenedithioacetal of Formula 22 with an ambident nucleophile of Formula 6 (Scheme 14). The nucleophiles of Formula 6 are described above.

Scheme 14

Ketene dithioacetals of Formula 22a or 22b can be prepared by condensing phenyl acetic acid esters of Formula 9 or amides of Formula 9a, respectively, with carbon disulfide in the presence of a suitable base, followed by reaction with two equivalents of an R^1 -halide, such as iodomethane or propargyl bromide (Scheme 15). Conversion of 22b to 22c can be accomplished by reaction with trialkyl tetrafluoroborates.

Scheme 15

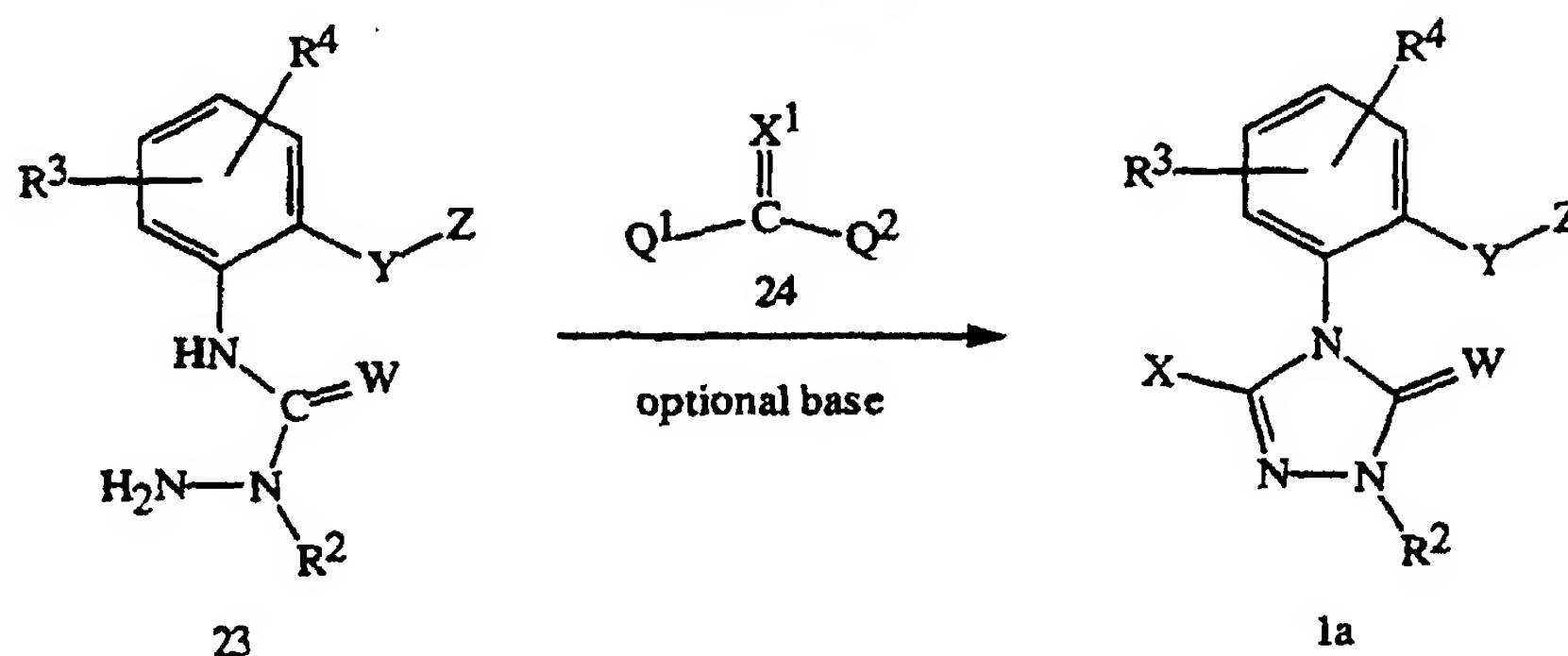
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Compounds of Formula 1a (compounds of Formula 1 wherein A = N and G = N) can be prepared by condensation of *N*-amino-ureas of Formula 23 with a carbonylating agent of Formula 24 (Scheme 16). The carbonylating agents of Formula 24 are carbonyl or thiocarbonyl transfer reagents such as phosgene, thiophosgene, diphosgene (ClC(=O)OCCl₃), triphosgene (Cl₃COC(=O)OCCl₃), *N,N'*-carbonyldiimidazole, *N,N'*-thiocarbonyldiimidazole, and 1,1'-carbonyldi(1,2,4-triazole). Alternatively, the compounds of Formula 24 can be alkyl chloroformates or dialkyl carbonates. Some of these carbonylating reactions may require the addition of a base to effect reaction. Appropriate bases include alkali metal alkoxides such as potassium *tert*-butoxide, inorganic bases such as sodium hydride and potassium carbonate, pyridine, or tertiary amines such as triethylamine, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or triethylenediamine. Suitable solvents include polar aprotic solvents such as acetonitrile, dimethylformamide, or dimethyl sulfoxide; ethers such as tetrahydrofuran, dimethoxyethane or diethyl ether; ketones such as acetone or 2-butanone; hydrocarbons such as toluene or benzene; or halocarbons such as dichloromethane or chloroform. The reaction temperature can vary between 0°C and 150°C and the reaction time can be from 1 to 72 hours depending on the choice of base, solvent, temperature, and substrates.

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Scheme 16



Q¹ and Q² are independently Cl, OCCl₃, O(C₁-C₄ alkyl), 1-imidazolyl, 1,2,4-triazolyl

X = OH or SH

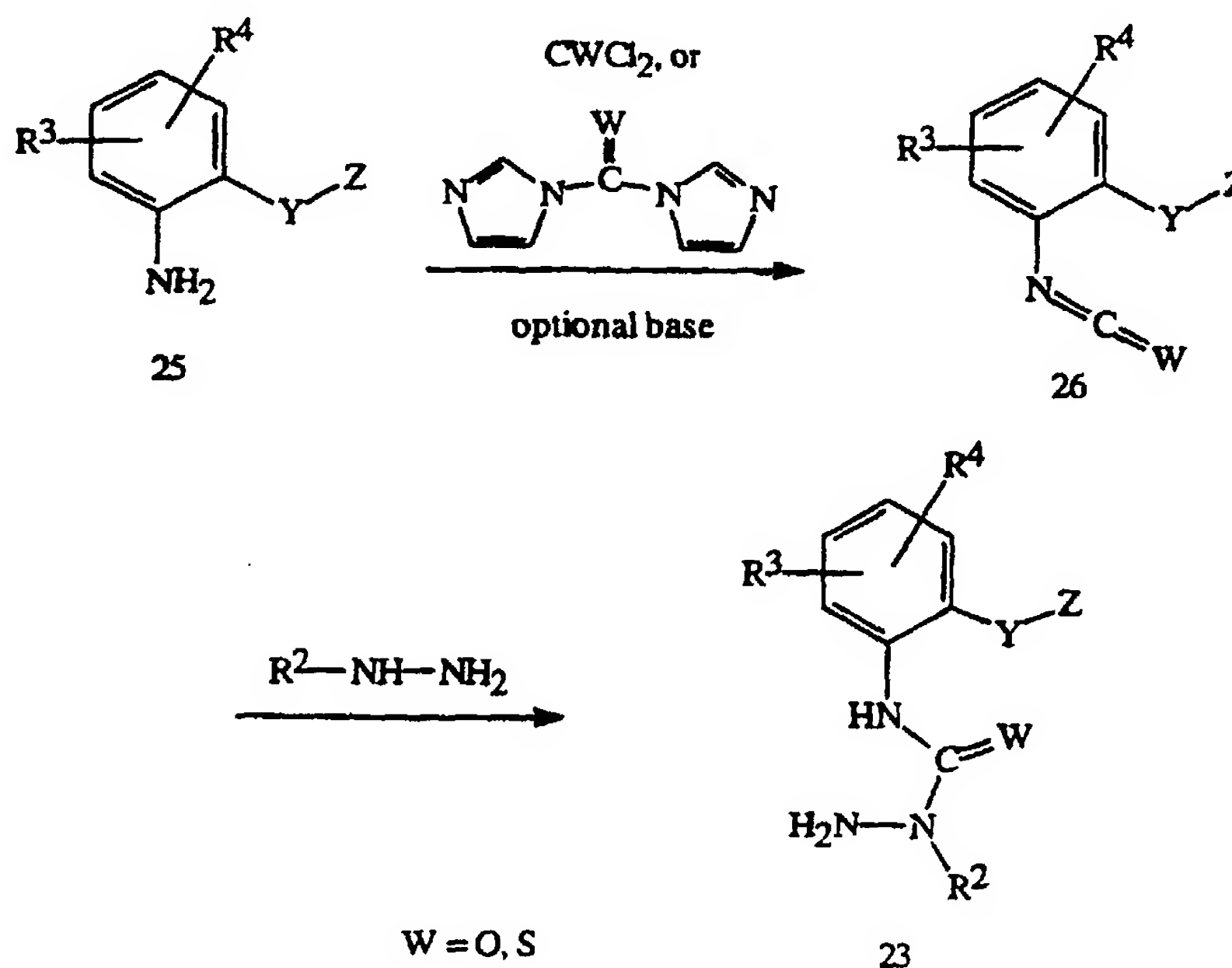
X¹ = O or S

N-Amino-ureas of Formula 23 can be prepared as illustrated in Scheme 17.

Treatment of an aniline of Formula 25 with phosgene, thiophosgene,

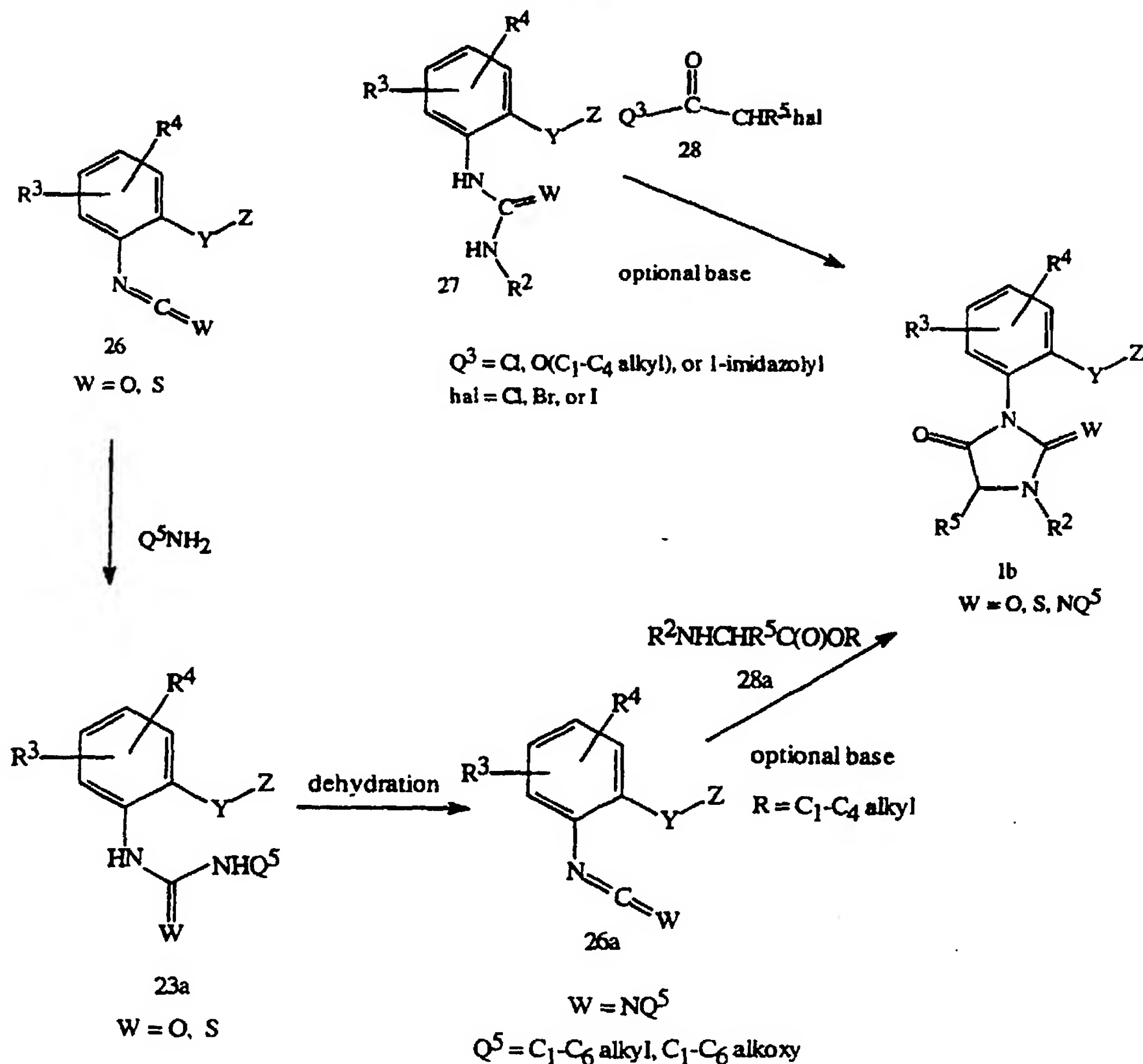
- 5 *N,N'*-carbonyldiimidazole, or *N,N'*-thiocarbonyldiimidazole produces the isocyanate or isothiocyanate of Formula 26. A base can be added for reactions with phosgene or thiophosgene. Subsequent treatment of the iso(thio)cyanate with an R²-substituted hydrazine produces the *N*-amino-urea of Formula 23.

Scheme 17



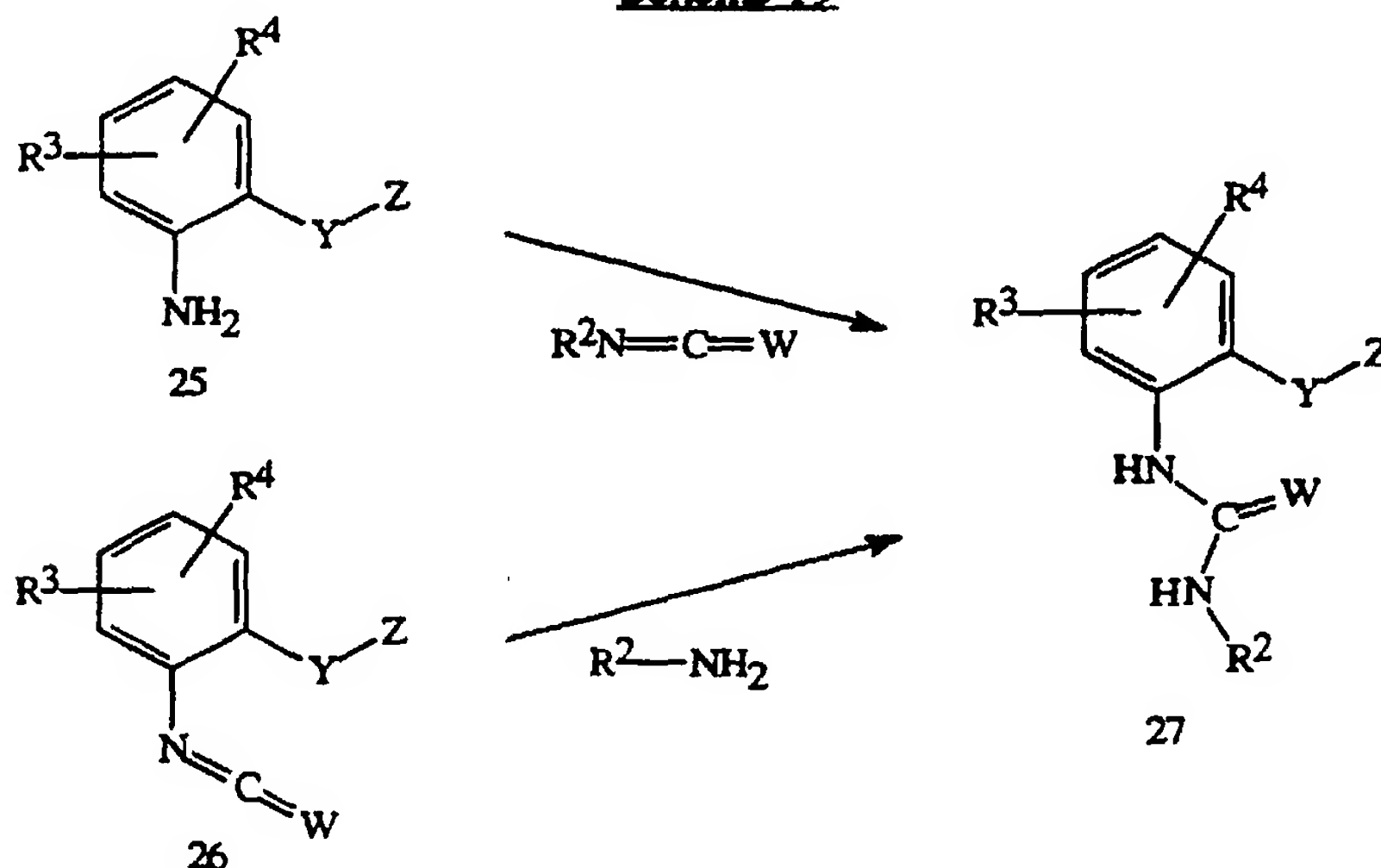
- Compounds of Formula 1b (compounds of Formula 1 wherein $A = CR^5$, $G = N$, and $X = O$) can be prepared by either method illustrated in Scheme 18. Ureas of Formula 27 are reacted with activated 2-halocarboxylic acid derivatives such as 2-halocarboxylic acid chlorides, 2-halocarboxylic acid esters or 2-haloacyl imidazoles.
- 5 The initial acylation on the aniline nitrogen is followed by an intramolecular displacement of the 2-halo group to effect cyclization. Base may be added to accelerate the acylation and/or the subsequent cyclization. Suitable bases include triethylamine and sodium hydride. Alternatively, Formula 1b compounds can be prepared by reaction of
- 10 Formula 26 iso(thio)cyanates or Formula 26a carbodiimides with Formula 28a esters. As described above, base may be added to accelerate the reaction and subsequent cyclization to Formula 1b compounds. Carbodiimides 26a can be prepared as shown in Scheme 18, starting with compounds of Formula 26.

Scheme 18



The (thio)ureas or amidines of Formula 27 can be prepared by either of the methods illustrated in Scheme 19. The anilines of Formula 25 can be contacted with an isocyanate or isothiocyanate of Formula $R^2N=C=W$ as described above. Alternatively, an iso(thio)cyanate of Formula 26 or carbodiimide of Formula 26a can be condensed with an amine of Formula R^2-NH_2 to form the urea or amidine. The anilines and iso(thio)cyanates of Formulae 25 and 26, respectively, are commercially available or prepared by well-known methods. For example, isothiocyanates can be prepared by methods described in *J. Heterocycl. Chem.*, (1990), 27, 407. Isocyanates can be prepared as described in March, *J. Advanced Organic Chemistry*; 3rd ed., John Wiley: New York, (1985), pp 944, 1166.

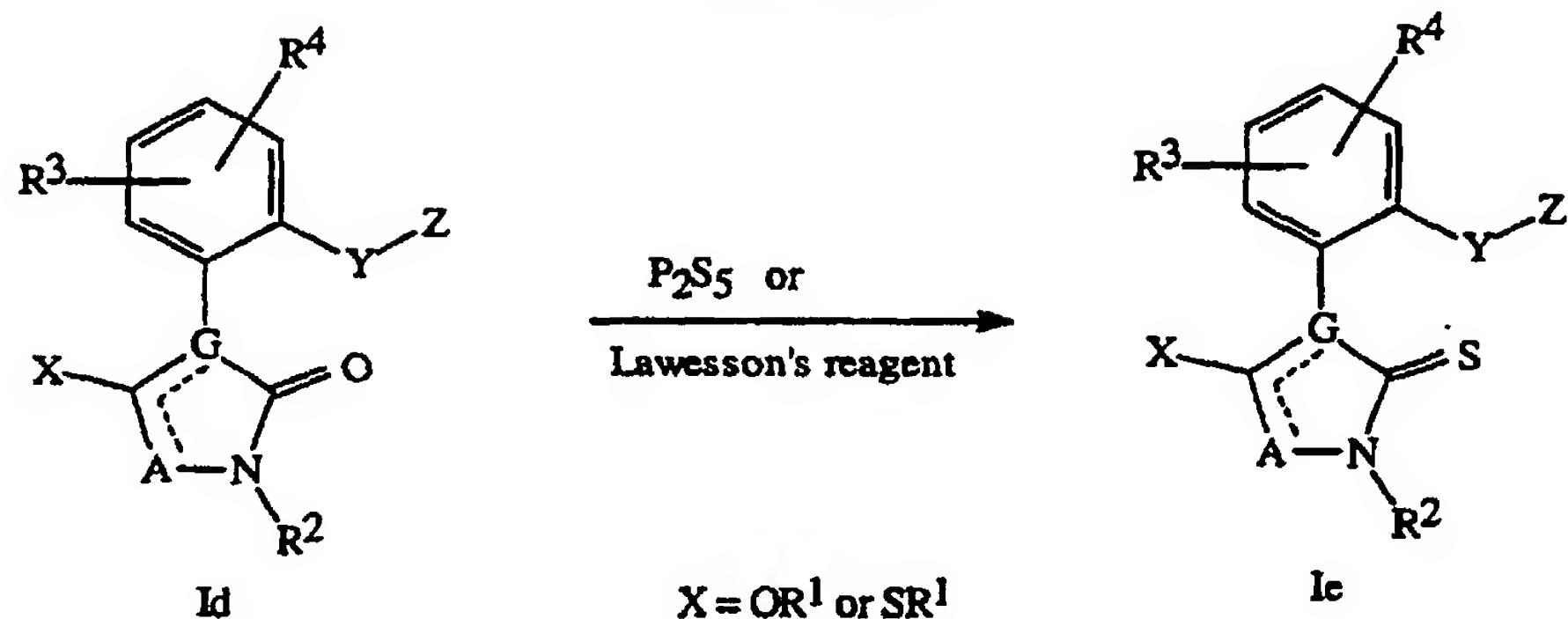
Scheme 19



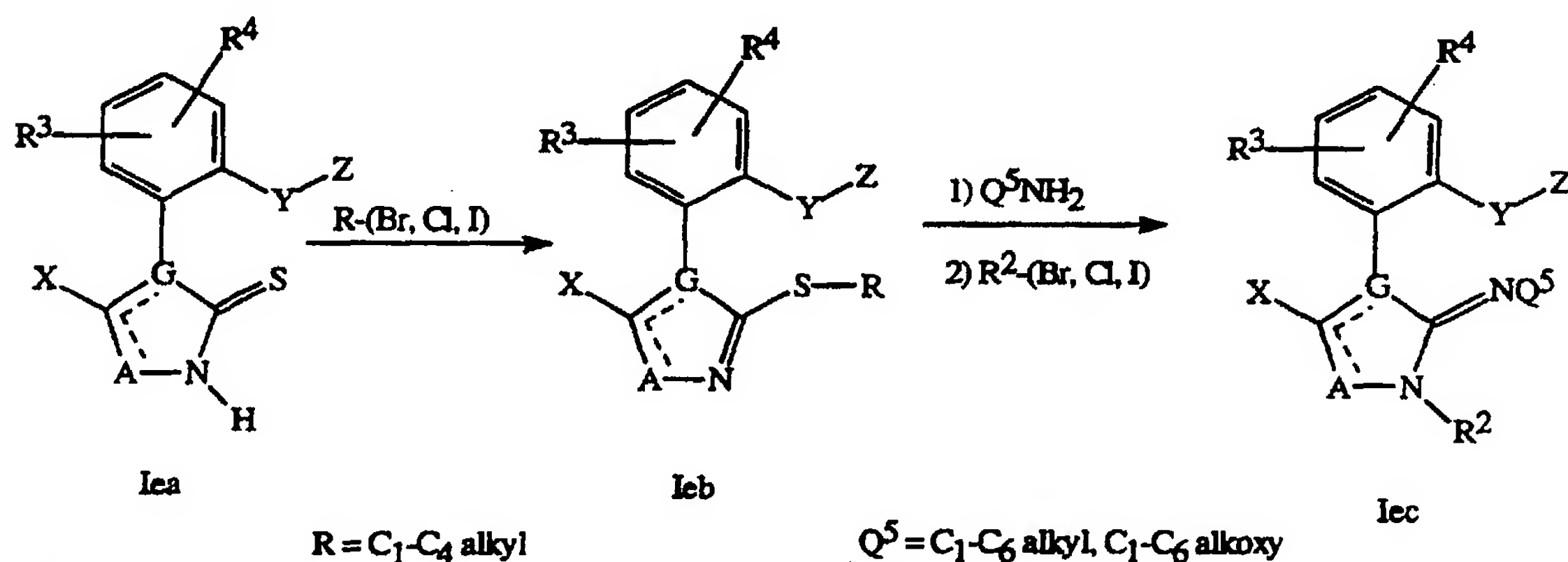
4) Thionation Procedures

Compounds of Formula 1e (compounds of Formula I wherein $W = S$) can be prepared by treating compounds of Formula Id (I wherein $W = O$) with thionating reagents such as P_2S_5 or Lawesson's reagent [2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide] as illustrated in Scheme 20 (see *Bull. Soc. Chim. Belg.*, (1978), 87, 229; and *Tetrahedron Lett.*, (1983), 24, 3815).

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Scheme 20

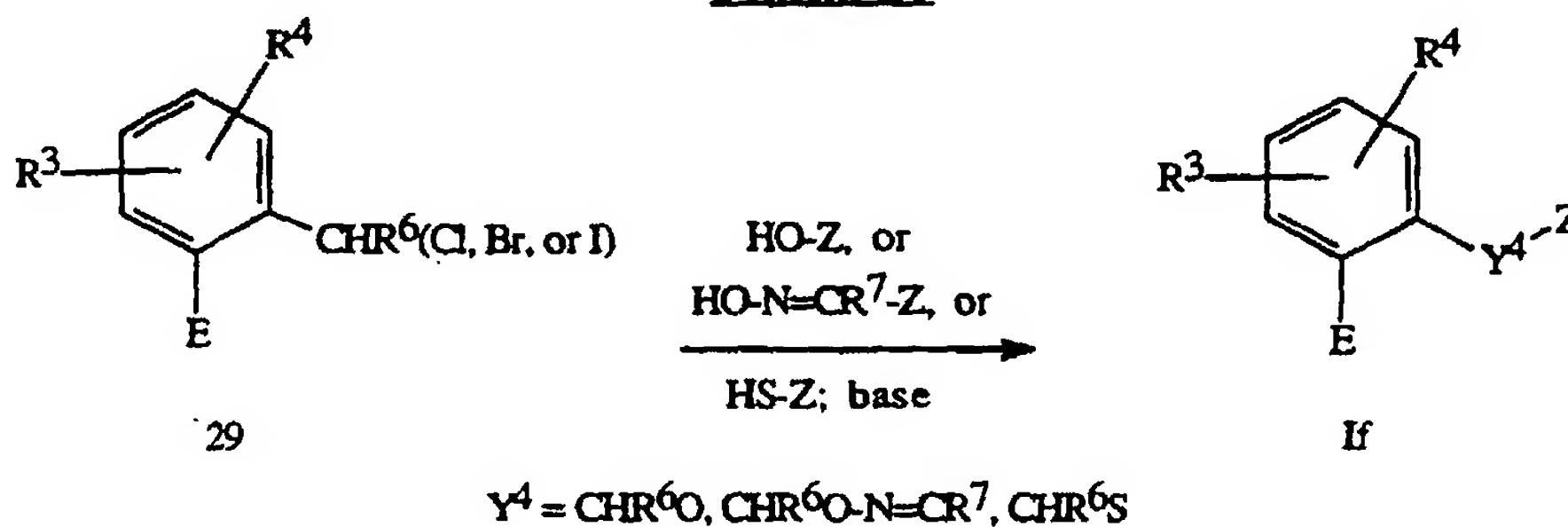
Reaction of compounds of Formula Iea with an alkyl halide in the presence of base provides compounds of Formula Ieb, which can be reacted with compounds of Formula Q^5NH_2 and then alkylated with $\text{R}^2\text{-(Br, Cl, or I)}$ to provide compounds of Formula Iec.

Scheme 20a5) Aryl Moiety Synthesis Procedures

Compounds of Formula If (compounds of Formula I wherein Y is CHR^6O , CHR^6S , or $\text{CHR}^6\text{O-N=CR}^7$) can be prepared by contacting benzyl halides of Formula 29 with various nucleophiles (Scheme 21). The appropriate alcohol or thiol is treated with a base, for example sodium hydride, to form the corresponding alkoxide or thioalkoxide which acts as the nucleophile. Compounds of Formula If (compounds of Formula I wherein $\text{E} = \text{E}^2$ and $\text{Y} = \text{Y}^4$ as defined in Scheme 21) can be prepared according to methods described in the following references: for $\text{Y}^4 = \text{CHR}^6\text{O}$, EP-A-278,595 and EP-A-472,224; for $\text{Y}^4 = \text{CHR}^6\text{S}$, EP-A-379,098; for $\text{Y}^4 = \text{CHR}^6\text{O-N=CR}^7$, EP-A-370,629 and WO 94/05620. Compounds of Formula If (compounds of Formula I

wherein $E = E^3$ and $Y = Y^4$ as defined in Scheme 21) can be prepared according to methods described in the following references: for $Y^4 = \text{CHR}^6\text{O}$, EP-A-253,213, EP-A-498,188 and EP-A-554,767; for $Y^4 = \text{CHR}^6\text{S}$, EP-A-374,811; for $Y^4 = \text{CHR}^6\text{O-N=CR}^7$, EP-A-414,153, EP-A-472,300, EP-A-515,901, and
 5 WO 92/18494.

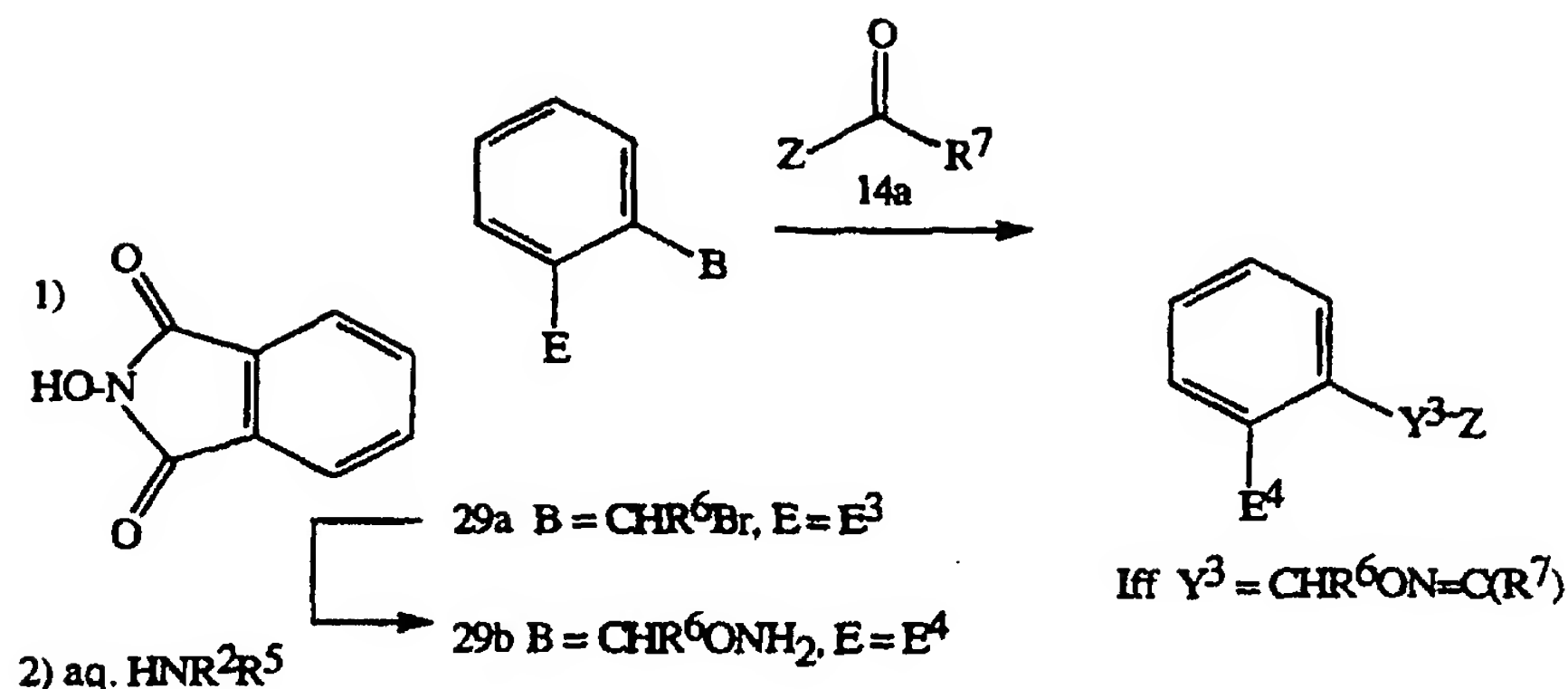
Scheme 21



Benzyl halides of Formula 29 can be prepared by radical halogenation of the
 10 corresponding alkyl compound (i.e., H instead of halogen in Formula 29), or by acidic
 cleavage of the corresponding methyl ether (i.e., OMe instead of halogen in Formula 29).
 Methods for preparing compounds of Formula 29 wherein $E = E^2$ are described in
 WO 94/05620. Methods for preparing compounds of Formula 29 wherein $E = E^3$ are
 described in EP-A-254,426, EP-A-299,694 and AU-A-55899/90. Compounds of
 15 Formula 29a wherein $E = E^3$ can be used to prepare compounds of Formula If wherein
 $E = E^4$ and $Y^4 = \text{CH}_2\text{R}^6\text{O-N=CR}^7$ according to methods described in EP-A-585,751
 and illustrated in Scheme 21a. Compounds of Formula 29a are treated with *N*-
 hydroxyphthalimide, followed by treatment with HNR^2R^5 to provide compounds of
 Formula 29b. Treatment of compounds of Formula 29b with compounds of
 20 Formula 14a provides compounds of Formula If.

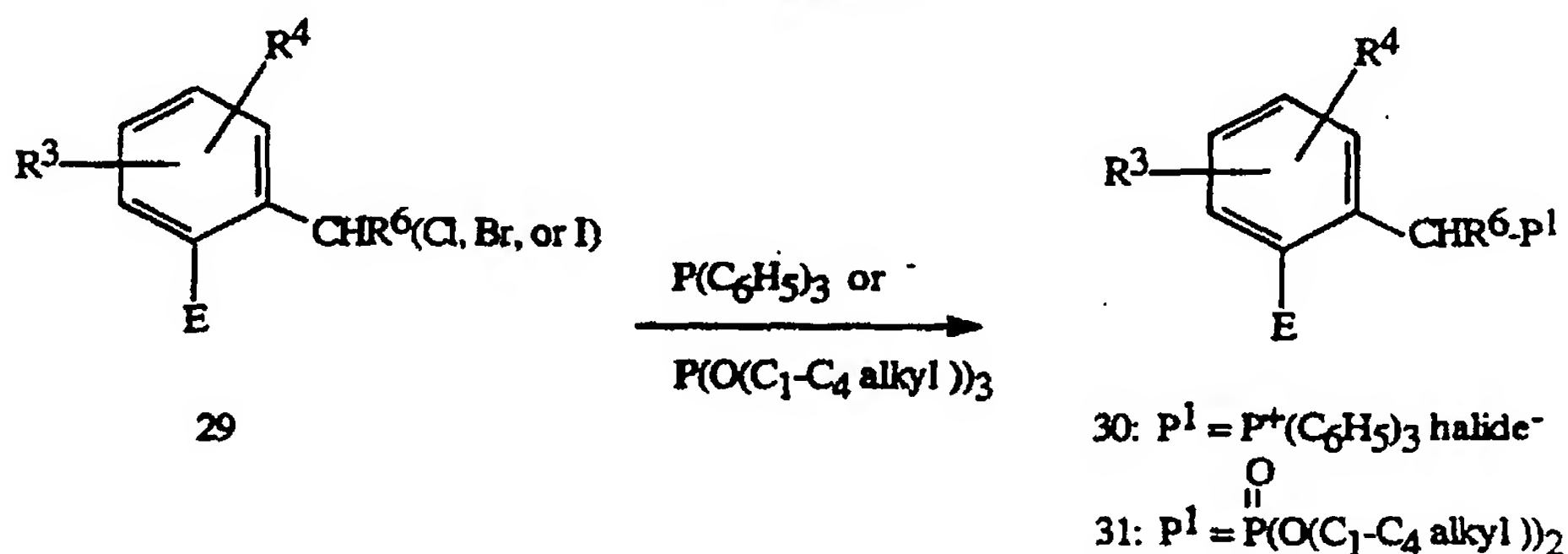
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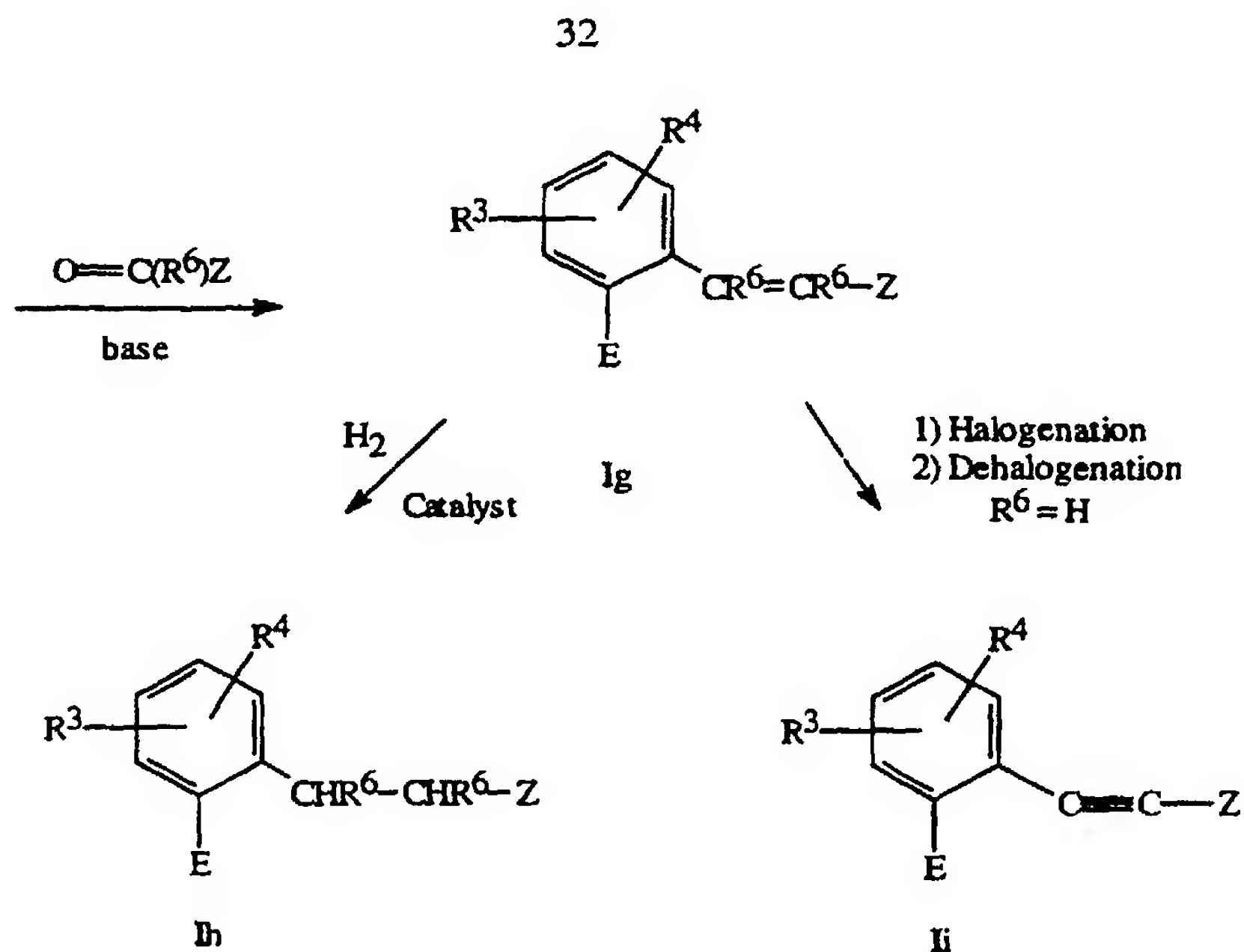
Scheme 21a



- Compounds of Formula I wherein Y is $\text{CR}^6=\text{CR}^6$ and $\text{CHR}^6-\text{CHR}^6$ (Formula Ig and Ih, respectively) can be prepared as illustrated in Scheme 22. Treatment of the benzyl halides of Formula 29 with triphenylphosphine or a trialkylphosphite produces the corresponding phosphonium salt (Formula 30) or phosphonate (Formula 31), respectively. Condensation of the phosphorus compound with a base and a carbonyl compound of Formula $\text{Z}(\text{R}^6)\text{C}=\text{O}$ affords the olefin of Formula Ig. Compounds of Formula Ig wherein $\text{E} = \text{E}^2$ may be prepared by methods described in EP-A-203,606, EP-A-474,042, EP-A-528,245 and FR 2,670,781. Compounds of Formula Ig wherein $\text{E} = \text{E}^3$ may be prepared by methods described in EP-A-253,213 and EP-A-254,426.

Scheme 22



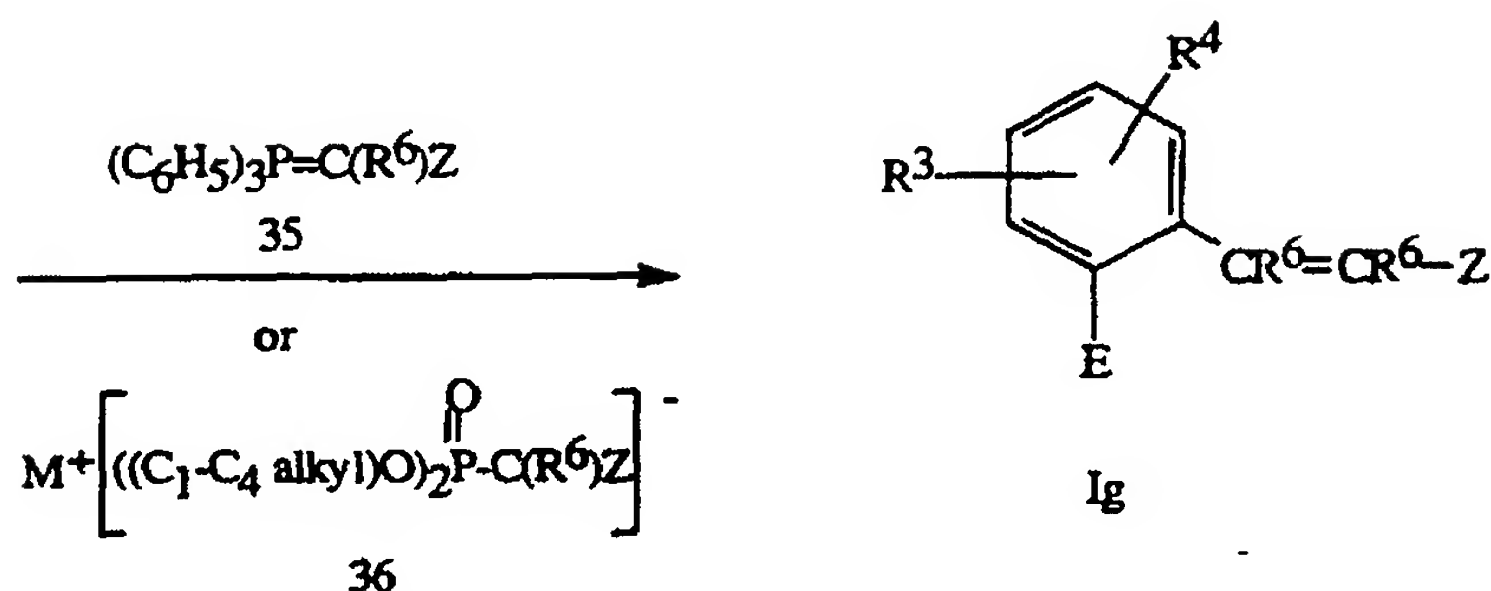
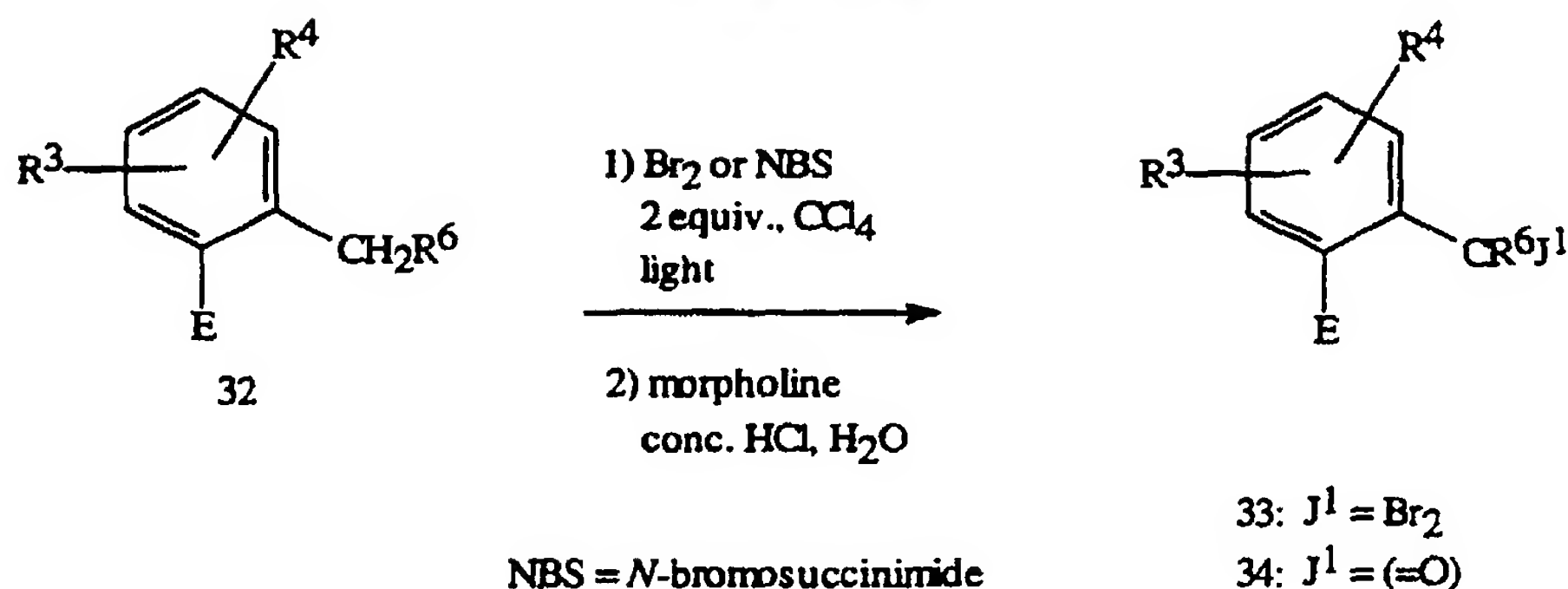


The olefins of Formula Ig can be converted to the saturated compounds of Formula Ih by hydrogenation over a metal catalyst such palladium on carbon as is well-known in the art (Rylander, *Catalytic Hydrogenation in Organic Synthesis*; Academic: New York, 1979). Compounds of Formula Ih wherein E = E² may be prepared by methods described in EP-A-178,826 and EP-A-229,974. Compounds of Formula Ih wherein E = E³ may be prepared by methods described in EP-A-253,213.

Formula Ii alkynes can be prepared by halogenation/dehalogenation of Formula Ig olefins using procedures well-known in the art (March, J. *Advanced Organic Chemistry*; 3rd ed., John Wiley: New York, (1985), p 924). Additionally, Formula Ii alkynes can be prepared by well-known reaction of aromatic halides with alkyne derivatives in the presence of catalysts such as nickel or palladium (see *J. Organomet. Chem.*, (1975), 93 253-257). Compounds of Formula Ii wherein E = E², E³, or E⁴ may be prepared by methods described in EP-A-178,826, EP-A-253,213 and EP-A-582,925.

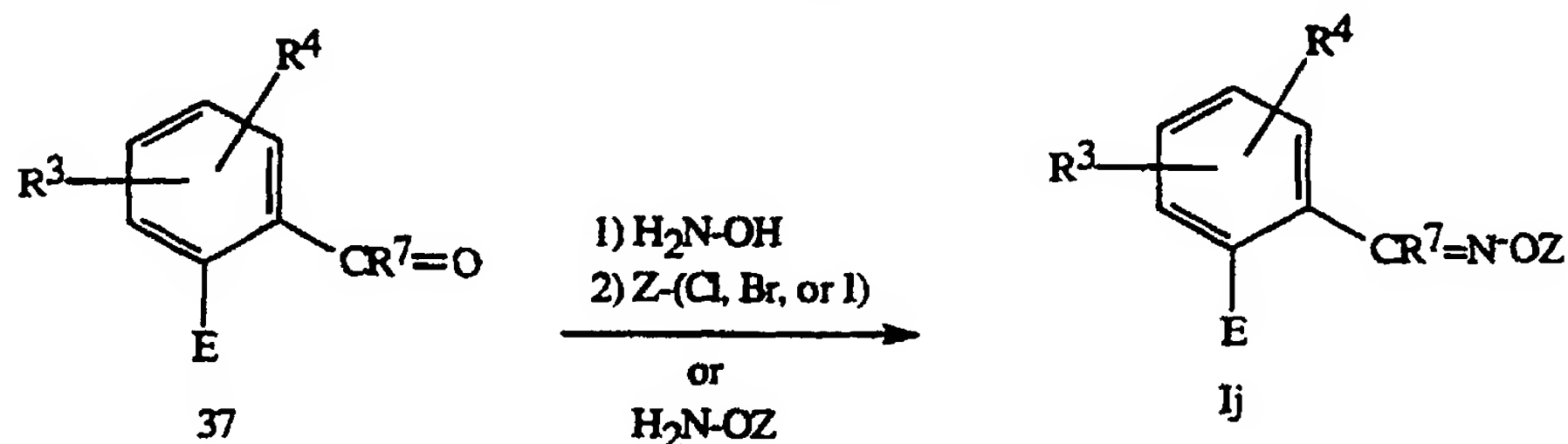
The olefin of Formula Ig can also be prepared by reversing the reactivity of the reactants in the Wittig or Horner-Emmons condensation. For example, 2-alkylphenyl derivatives of Formula 31 can be converted into the corresponding dibromo-compounds of Formula 33 as illustrated in Scheme 23 (see *Synthesis*, (1988), 330). The dibromo-compounds can be hydrolyzed to the carbonyl compounds of Formula 34, which in turn can be condensed with a phosphorus-containing nucleophile of Formula 35 or 36 to afford the olefins of Formula Ig.

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Scheme 23

- Oximes of Formula Ij (Formula I wherein Y is C(R⁷)=N-O) can be prepared from carbonyl compounds of Formula 37 by condensation with hydroxylamine, followed by *O*-alkylation with electrophiles of Formula Z-(Cl, Br, or I) (Scheme 24). Alternatively, the *O*-substituted hydroxylamine can be condensed with the carbonyl compound of Formula 37 to yield oximes of Formula Ij directly. Compounds of Formula Ij wherein E = E², E³, or E⁴ may be prepared by methods described in EP-A-499,823 and EP-A-596,254.

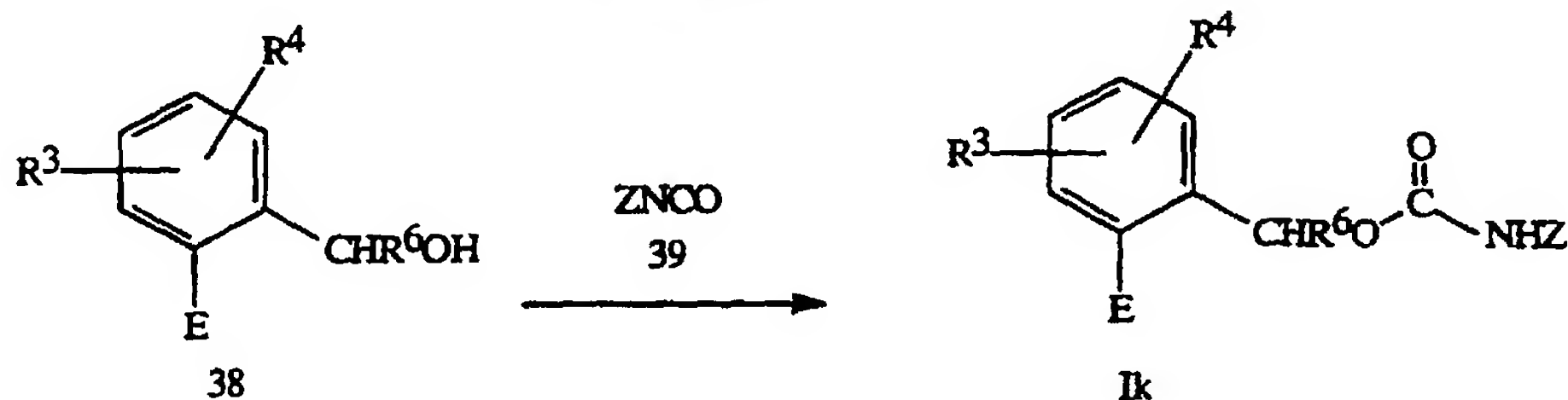
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Scheme 24

Carbamates of Formula Ik can be prepared by reacting benzyl alcohols of Formula 38 with isocyanates of Formula 39 (Scheme 25). A base such as triethylamine

can be added to catalyze the reaction. Compounds of Formula Ik wherein E = E², E³, or E⁴ may be prepared by methods described in WO 93/07116.

Scheme 25



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Compounds of Formula II wherein E = E² or E³ and Y⁵ = -O- may be prepared by methods described in EP-A-178,826, EP-A-341,845 and EP-A-464,381. Compounds of Formula II wherein E = E² and Y⁵ = -S- may be prepared by methods described in GB 2,218,702. Compounds of Formula II wherein E = E² and Y⁵ = -OCH₂- may be prepared by methods described in EP-A-203,608 and EP-A-402,246.

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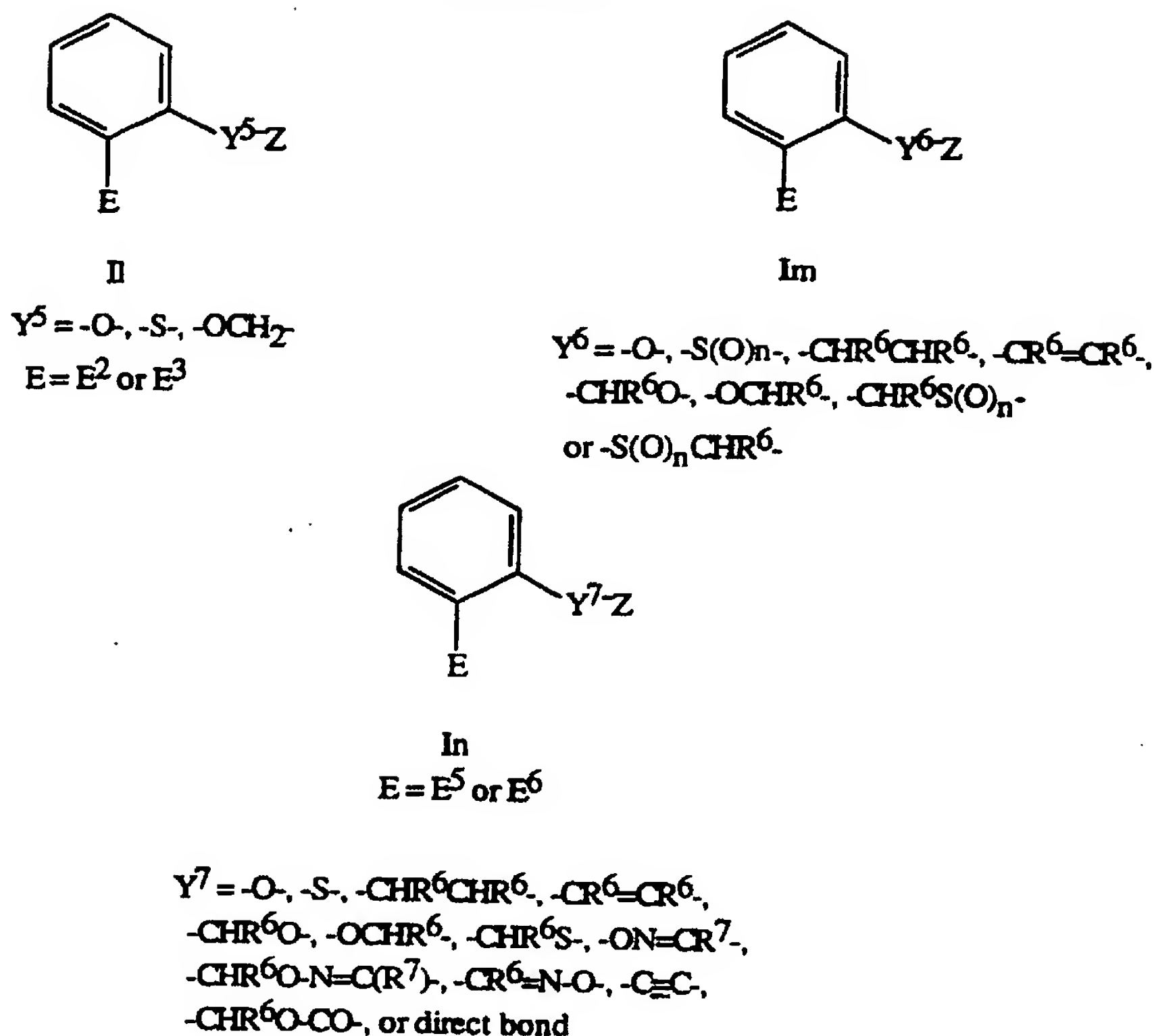
Compounds of Formula Im wherein E = E⁴ and Y⁶ is as defined in Scheme 26 may be prepared by methods described in EP-A-398,692.

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Compounds of Formula In wherein E = E⁵ or E⁶ and Y⁷ is as defined in Scheme 26 may be prepared by methods described in WO 93/15046. Compounds of Formula In wherein E = E⁵ and Y⁷ = -CHR⁶O-N=C(R⁷)- may be prepared by methods described in JP 94/056756, JP 94/025142 and EP-A-498,396.

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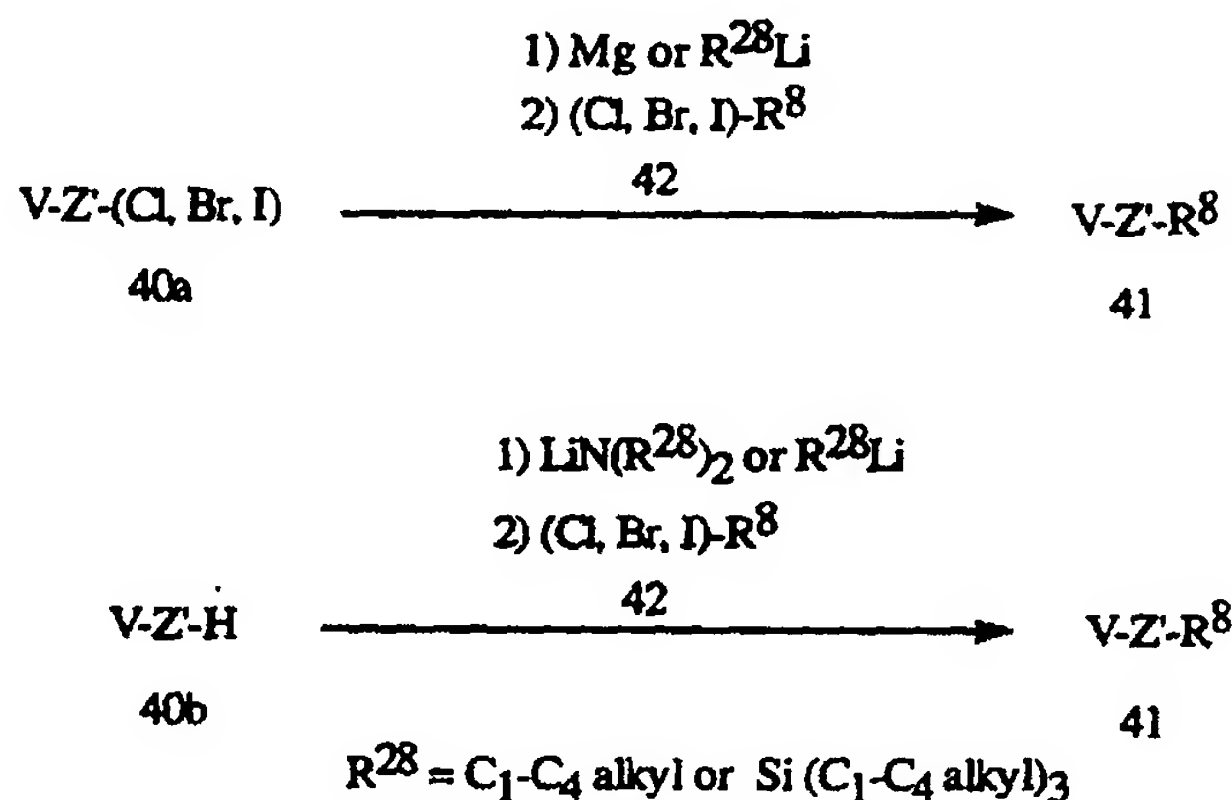
Scheme 26



The silyl- or germyl-containing compounds of the present invention are prepared by combinations of reactions as illustrated in the Schemes 1-26 in which Z is a moiety as described in the summary, substituted with $R^8 = SiR^{19}R^{20}R^{21}$ or $GeR^{19}R^{20}R^{21}$. Silicon- or germanium-containing compounds can be prepared using methods well-known in the art. (For leading references on the art of preparing silyl- and germyl-substituted compounds, see *The Organic Compounds of Germanium*, Michel Lesabre, Pierre Mazerolles, and Jacques Satgé, Dietmar Seyferth, ed., John Wiley & Sons, NY; C. Eaborn and K. C. Pande, *J. Chem. Soc.* (1960) 3200-3203; M. Wieber and M. Schmidt, *J. Organometal. Chem.* (1963) 93-94; and WO 94/08976). See Scheme 27 for two methods. In Scheme 27, Z' = the radical Z as described in the summary, unsubstituted with R^8 ; V = any group attached to Z as depicted in each of the individual schemes. (See the following paragraph for some examples of how V is defined in individual schemes.) One method is the reductive metallation or halogen-metal exchange of a halogen-substituted V-Z' of Formula 40a using magnesium or an organolithium reagent, followed by treatment with a silyl- or germyl-substituted halide of Formula 42. A second method is deprotonation of compounds of Formula 40b using a strong base such as a lithioamide or an organolithium reagent, followed by treatment with a silyl- or

germyl-halide of Formula 42. One skilled in the art will recognize that these methods may require protection and deprotection sequences for certain V moieties which may be incompatible with the reagents. See the preparation of Intermediate 1 in the Examples for an example of a protection-deprotection strategy. One skilled in the art would also
 5 recognize that, in some cases, additional synthetic steps after the introduction of R⁸ would be necessary to prepare a particular V group as it is depicted in any individual scheme. See the preparation of Intermediate 2 in the Examples for an example of this strategy.

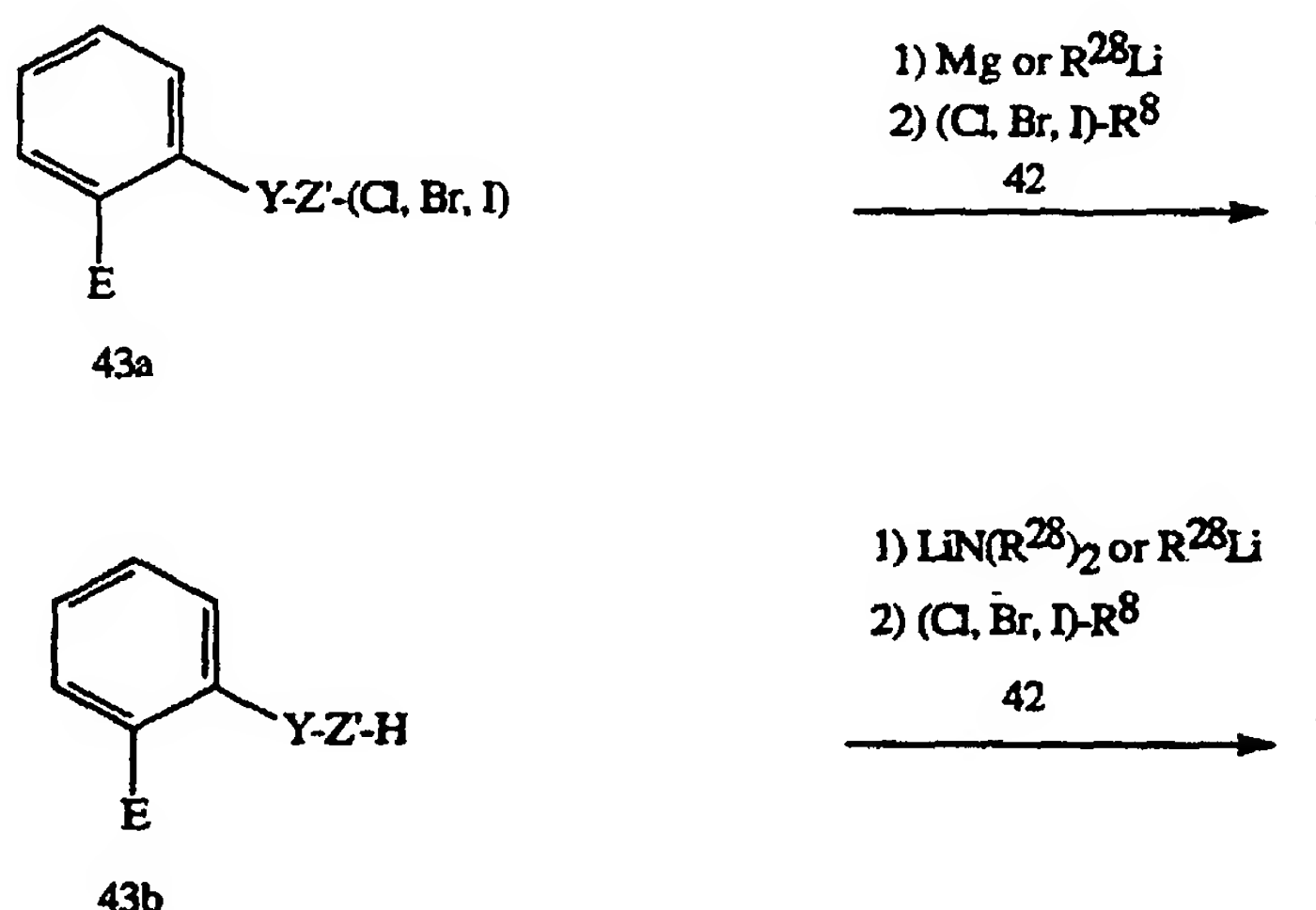
Scheme 27



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One skilled in the art will recognize that the best method and timing of the introduction of R⁸ will be dependent on the molecular composition of the particular compound of Formula I desired. In some cases, the introduction of R⁸ would occur on
 15 an intermediate of Formula 40a or b (see Scheme 27) to provide an intermediate of Formula 41 which would be coupled to another moiety to provide a third molecule which could be elaborated further to provide compounds of Formula I. For example, V in Scheme 27 would correspond to the HO-, HON = CR⁷- or HS-substituents in Scheme 21 (or their synthetic precursors), attached to Z to define the nucleophiles which are reacted
 20 with Formula 29 to provide Formula If. In another example, Formula 41 would correspond to Formula 14a in Scheme 8, where V = -C(=O)R⁷. In other cases, R⁸ can be introduced as a substituent on a reagent of Formula 41 which can be elaborated further to provide the compounds of this invention or their precursors. For example, in Scheme 3, if Y = direct bond, -O-, -S(O)_n-, NR⁶, C(=O), CHOR⁶, or CHR⁶ and
 25 Z = phenyl substituted with R⁸, a compound of Formula 8 can be prepared from a compound of Formula 40a (in which Z' = phenyl and V = phenyl-direct bond-, phenyl-O-, phenyl-S(O)_n-, phenyl-NR⁶-, phenyl-C(=O)-, phenyl-CHGR⁶-, or

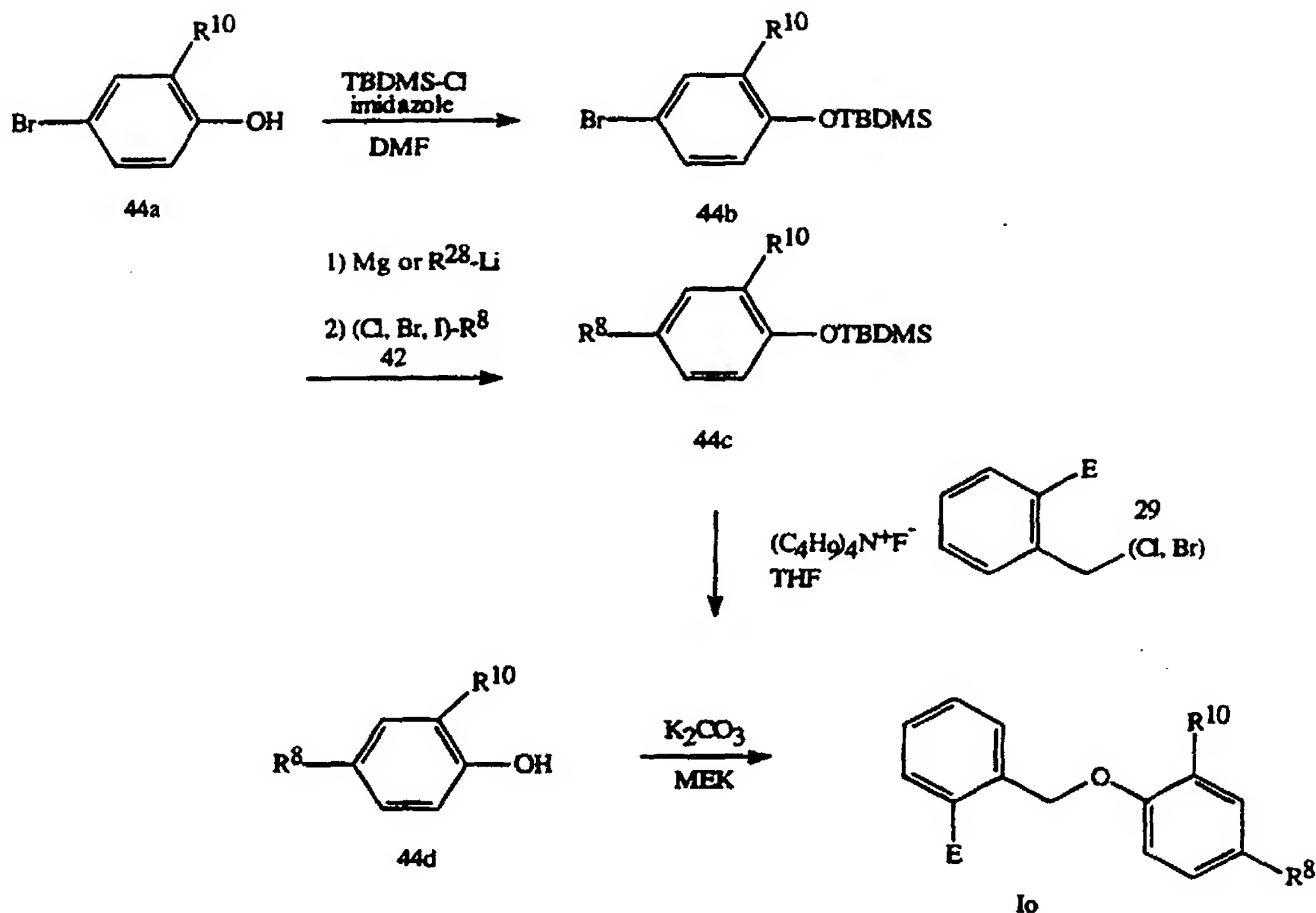
phenyl-CHR⁶-) by the method in Scheme 27, followed by iodination. A more specific illustration of the strategy for introduction of R⁸ into compounds of Formula I is shown in Scheme 29 (see below). This Scheme illustrates an example of preparation of Z-OH in Scheme 21 followed by coupling to give compounds of the invention. Finally, R⁸ can be introduced as the final step in which compounds of Formula I are prepared from compounds of Formula 42a or b (see Scheme 28).

Scheme 28

Compounds of Formula Io can be made using a protection/deprotection scheme to prepare the requisite phenols of Formula 44d. Protection of the halophenol, followed by electrophilic substitution by R⁸ and then deprotection yields compounds of Formula 44d which are coupled to compounds of Formula 29 in refluxing methyl ethyl ketone (MEK, or a similar solvent) in the presence of a base (preferably potassium carbonate) to give compounds of Formula Io.

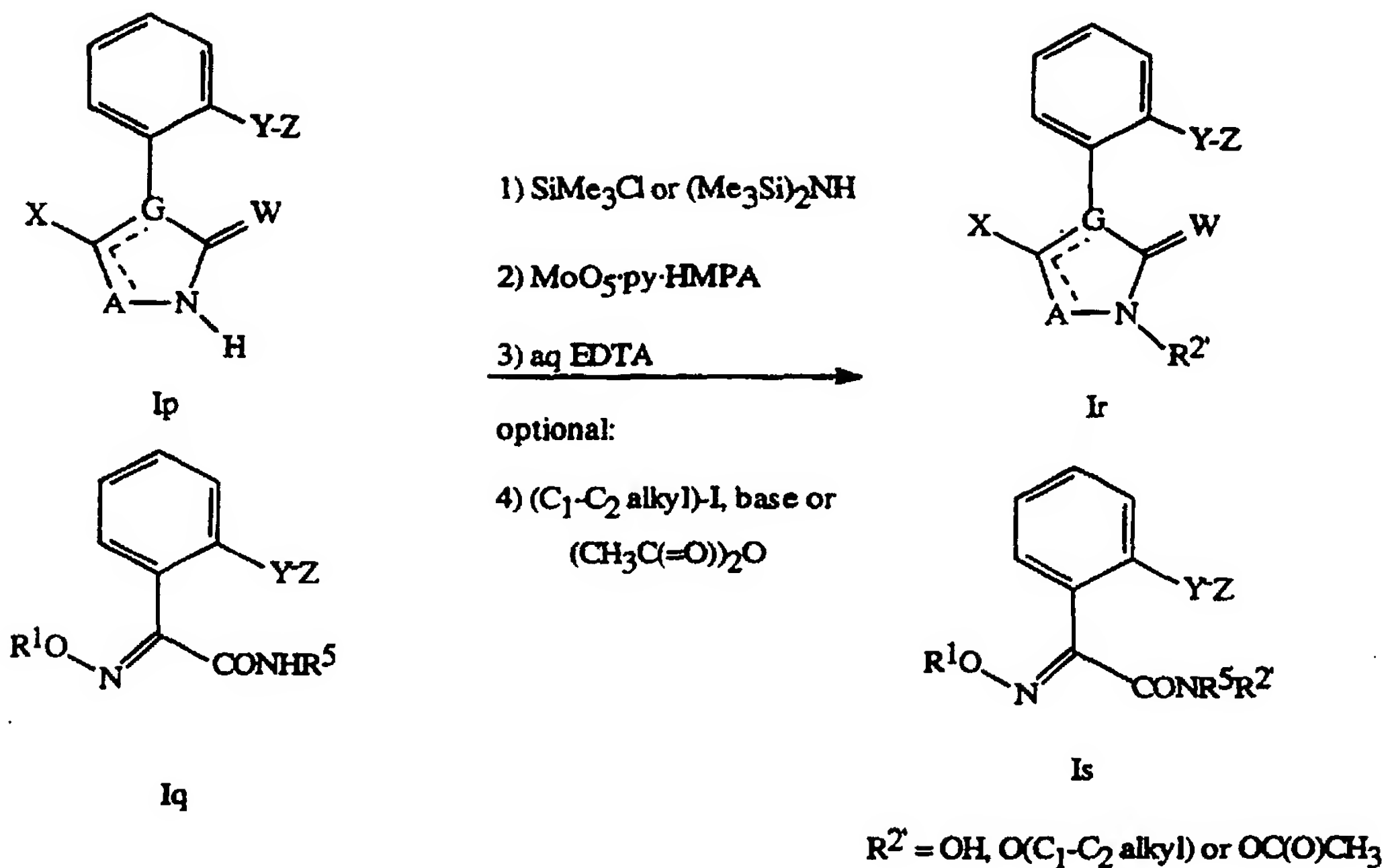
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Scheme 29



Conversion of compounds of Formula Ip and Iq to compounds of Formula Ir and Is, respectively, is summarized in Scheme 30. Reaction of the secondary amides with silylating agents, such as trimethylsilyl chloride in the presence of base or hexamethyldisilazane in the presence of acid, provides the silylated intermediate which is oxidized *in situ* with the peroxo-molybdenum compound MoO_5 -HMPA complexed with pyridine or dimethylformamide. Subsequent hydrolysis with aqueous EDTA (ethylenediaminetetraacetic acid) liberates the hydroxylated amides (see S. A. Martin, P. G. Sammes and R. M. Upton, *J. Chem. Soc., Perkin Trans. 1*, (1979), 2481 and J. H. Rigby and M. Qabar, *J. Org. Chem.*, (1989), 54, 5852). Optional alkylation with C_1 - C_2 alkyl halides in the presence of base or acylation with acetic anhydride can be performed on the hydroxyl amides Ir and Is where $R^{2'} = OH$.

Scheme 30



It is recognized that some reagents and reaction conditions described above for preparing compounds of Formula I may not be compatible with certain functionalities present in the intermediates. In these instances, the incorporation of protection/deprotection sequences or functional group interconversions into the synthesis will aid in obtaining the desired products. The use and choice of the protecting groups will be apparent to one skilled in chemical synthesis (see, for example, Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 2nd ed.; Wiley: New York, 1991). One skilled in the art will recognize that, in some cases, after the introduction of a given reagent as it is depicted in any individual scheme, it may be necessary to perform additional routine synthetic steps not described in detail to complete the synthesis of compounds of Formula I.

One skilled in the art will also recognize that compounds of Formula I and the intermediates described herein can be subjected to various electrophilic, nucleophilic, radical, organometallic, oxidation, and reduction reactions to add substituents or modify existing substituents.

Without further elaboration, it is believed that one skilled in the art using the preceding description can utilize the present invention to its fullest extent. The following Examples are, therefore, to be construed as merely illustrative, and not limiting of the disclosure in any way whatsoever. Percentages are by weight except for

chromatographic solvent mixtures or where otherwise indicated. Parts and percentages for chromatographic solvent mixtures are by volume unless otherwise indicated.

¹H NMR spectra are reported in ppm downfield from tetramethylsilane; s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, br s = broad singlet.

EXAMPLE 1

Step A: Methyl 2-(bromomethyl)benzeneacetate

Methyl *o*-tolylacetate (24 g), *N*-bromosuccinimide (27.2 g) and benzoyl peroxide (~ 50 mg) were mixed in 200 mL of carbon tetrachloride and heated to reflux with a high-intensity light source for 1.5 h. After cooling, the precipitate was removed by filtration and the filtrate concentrated *in vacuo* to yield 36 g (~100% yield) of the title compound of Step A as an amber oil. ¹H NMR (CDCl₃): δ 7.34 (m,1H), 7.26 (m,2H), 7.16 (m,1H), 4.57 (s,2H), 3.80 (s,2H), 3.69 (s,3H).

Step B: Methyl 2-[(benzoylamino)oxy]methylbenzeneacetate

Benzohydroxamic acid (17 g) and potassium carbonate (18.7 g) were suspended in 200 mL of acetonitrile and the mixture was stirred at 60°C for 30 min. A solution of 28 g of the title compound of Step A in 100 mL of acetonitrile was added dropwise over 0.5 h. The mixture was stirred at 60°C for 3 h and then cooled to room temperature overnight. Heating was resumed for an additional 4 h. The mixture was cooled and filtered. The filtrate was concentrated *in vacuo*. The residue was taken up in 200 mL of ethyl acetate and washed with 100 mL of 6% aqueous potassium carbonate solution. The aqueous wash was extracted with 100 mL of ethyl acetate. The combined organic phases were washed with 100 mL of water. The organic phase was dried (MgSO₄), filtered and concentrated *in vacuo* to yield 31.5 g (93% yield) of the title compound of Step B as an orange oil. ¹H NMR (CDCl₃): δ 9.09 (br s,1H), 7.60 (m,2H), 7.47 (m,1H), 7.37 (m,3H), 7.29 (m,3H), 5.14 (s,2H), 3.88 (s,2H), 3.71 (s,3H).

Step C: Methyl 2-[(aminooxy)methyl]benzeneacetate hydrochloride

The title compound of Step B (31.5 g) was added to a solution of HCl in methanol (prepared by adding 20 mL of acetyl chloride slowly to 200 mL of methanol). The mixture was heated to 60°C for 1.5 h. The solvent was removed *in vacuo*. The residue was taken up in 100 mL of diethyl ether and stirred at room temperature for 30 min. The ether was decanted off and the solid was taken up in 100 mL of tetrahydrofuran and heated to -50°C. The mixture was then cooled in an ice water bath and the solid collected by filtration to provide 11.5 g (47% yield) of the title compound of Step C as a white solid melting at 169-170°C.

Step D: Methyl 2-[[[[1-[3-**(trimethylsilyl)phenyl]ethylidene]amino]oxy]methyl]benzeneacetate**

1-[3-(Trimethylsilyl)phenyl]ethanone (Intermediate 1, 1.15 g) and the title compound of Step C (1.39 g) were dissolved in 40 mL of pyridine. The solution was heated to 90°C for 6 h, then cooled to room temperature overnight. The pyridine was removed *in vacuo* and the residue taken up in 40 mL of 1N HCl solution and extracted with ethyl acetate (3X50 mL). The combined organic layers were dried (MgSO₄), filtered and concentrated *in vacuo* to yield 2.1 g (95% yield) of the title compound of Step D as an amber oil. ¹H NMR (CDCl₃): δ 7.74 (s,1H), 7.59 (m,1H), 7.48 (m,2H), 7.31 (m,4H), 5.28 (s,2H), 3.83 (s,2H), 3.68 (s,3H), 2.23 (s,3H), 0.28 (s,9H).

Step E: Dimethyl [2-[[[[1-[3-**(trimethylsilyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]propanedioate**

The title compound of Step D (2.1 g) was dissolved in 10 mL of dimethyl carbonate. A slurry of 455 mg of sodium hydride (60% oil dispersion) in 10 mL of tetrahydrofuran was added and the mixture was heated to reflux 3 h. The mixture was cooled, quenched with 15 mL of 1N HCl solution and extracted with ethyl acetate (3x25 mL). The combined organic layers were dried (MgSO₄), filtered and concentrated *in vacuo* to yield 2.8 g of crude product, the title compound of Step E, as an amber oil. ¹H NMR (CDCl₃): δ 7.74 (s,1H), 7.55 (m,3H), 7.38 (m,4H), 5.28 (s,2H), 5.24 (s,1H), 3.72 (s,6H), 2.2 (s,3H), 0.28 (s,9H).

Step F: 5-Methoxy-2-methyl-4-[2-[[[[1-[3-**(trimethylsilyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3(2H)-isoxazolone**

N-methylhydroxylamine hydrochloride (1.43 g) was dissolved in 25 mL of methanol. A solution of 1.92 g of potassium hydroxide dissolved in 25 mL of methanol was added while cooling the reaction mixture with an ice bath. After 15 minutes, the precipitated potassium chloride was removed by filtration. To the filtrate was added a solution of 2.8 g of the title compound of Step E in 10 mL of methanol. The resulting mixture was stirred at room temperature overnight. The mixture was diluted with water, acidified with HCl and extracted with methylene chloride (3x30 mL). The combined organic layers were dried (MgSO₄), filtered and concentrated *in vacuo* to yield 2.35 g of an amber oil which was dissolved in 30 mL of toluene and 3 mL of methanol. A solution of 10% trimethylsilyldiazomethane in hexane (4 mL) was added dropwise and the solution was stirred at room temperature for 4 h. The solvents were removed *in vacuo* and the residue was purified by flash chromatography (1:1 hexane: ethyl acetate as eluent). The second eluting component was collected to yield 430 mg (19% yield) of the title compound of Step F, a compound of the invention, as an amber oil. ¹H NMR (CDCl₃): δ 7.72 (s,1H), 7.54 (m,3H), 7.34 (m,4H), 5.28 (s,2H), 3.91 (s,3H), 3.42 (s,3H), 2.24 (s,3H), 0.27 (s,9H).

EXAMPLE 2**Step A: 2,2-Dimethyl-N-(2-methylphenyl)hydrazinecarboxamide**

o-Tolyl isocyanate (10.0 g) was dissolved in 75 mL of toluene under nitrogen. The solution was cooled to 5°C and to this solution was slowly added a solution in toluene of 1,1-dimethylhydrazine (5.7 mL). After the addition, the ice-bath was removed and the resulting slurry allowed to stir an additional 10 minutes. The solid was filtered off and rinsed successively with hexane, a small amount of 20% diethyl ether/hexane, and then hexanes again. This afforded 11.1 g (77%) of the title compound of Step A. ¹H NMR (CDCl₃): δ 8.1 (br s, 1H), 7.94 (d, 1H), 7.21-7.15 (m, 3H), 6.99 (t, 1H), 5.23 (br s, 1H), 2.63 (s, 6H), 2.27 (s, 3H).

Step B: 5-Chloro 2,4-dihydro-2-methyl-4-(2-methylphenyl)-3H-1,2,4-triazol-3-one

To a solution of 11.1 g of the title compound of Step A dissolved in 600 mL methylene chloride under nitrogen was added 17.1 g of triphosgene. The solution was heated at reflux overnight, cooled, and then concentrated under reduced pressure. The resulting residue was dissolved in ethyl acetate, washed with water, and then washed with saturated aqueous NaCl. The organic phase was dried (MgSO₄), filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (30-50% ethyl acetate/hexanes as eluent) to afford 8.25 g (64%) of the title compound of Step B. ¹H NMR (CDCl₃): δ 7.42-7.30 (m, 3H), 7.17 (d, 1H), 3.54 (s, 3H), 2.22 (s, 3H).

Step C: 2,4-Dihydro-5-methoxy-2-methyl-4-(2-methylphenyl)-3H-1,2,4-triazol-3-one

8.25 g of the title compound of Step B was dissolved in 80 mL of 1:1 dimethoxyethane/methanol under nitrogen. 14.0 mL of sodium methoxide (30% solution in methanol) was added and the solution was heated at reflux for 3 h. The mixture was allowed to cool, diluted with ethyl acetate, washed with water, and then washed with saturated aqueous NaCl. The combined organic extracts were dried (MgSO₄), filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (50-70% ethyl acetate/hexanes as eluent) and triturated with 50% diethyl ether/hexanes to afford 6.7 g of the title compound of Step C (95% pure). ¹H NMR (CDCl₃): δ 7.35-7.27 (m, 3H), 7.18 (d, 1H), 3.94 (s, 3H), 3.46 (s, 3H), 2.22 (s, 3H).

Step D: 4-[2-(Bromomethyl)phenyl]-2,4-dihydro-5-methoxy-2-methyl-3H-1,2,4-triazol-3-one

To a solution/suspension of 6.7 g of the title compound of Step C dissolved in 95 mL of carbon tetrachloride under nitrogen was added *N*-bromosuccinimide (6.53 g) followed by a catalytic amount of benzoyl peroxide. The solution was heated at reflux for 2 h. Another 1.63 g of *N*-bromosuccinimide and a catalytic amount of benzoyl peroxide were added and the solution was heated at reflux for an hour. After cooling, methylene chloride was added and the organic layer was washed successively with water, 0.1 N

sodium thiosulfate solution, and then saturated aqueous NaCl. The combined organic extracts were dried (MgSO₄), filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (3-10% diethyl ether/methylene chloride as eluent) to afford 3.12 g of the title compound of Step D. ¹H NMR (CDCl₃):

5 δ 7.5 (m,1H), 7.44 (m,2H), 7.22 (m,1H), 4.60 (d,1H), 4.36 (d,1H), 3.96 (s,3H),
3.47 (s,3H).

Step E: 2,4-Dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-(trimethylsilyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3H-1,2,4-triazol-3-one

10 To a suspension of 5.22 g of 1-[3-(trimethylsilyl)phenyl]ethanone oxime (Intermediate 2) (21.0 mmol) in 40 mL of DMF was added 0.910 g (22.8 mmol) of 60% NaH (dispersion in oil) followed by 4.35 g (17.5 mmol) of the title compound of Step D. The reaction mixture was stirred at room temperature for 16 h then worked up by washing successively with water and brine, and then extracting with ethyl acetate.

15 The combined organic extracts were dried over MgSO₄, filtered and concentrated. The crude product was purified by flash chromatography on silica gel using 40% ethyl acetate/hexane as eluent to give 4.32 g (10.17 mmol, 58% yield) of the title compound of Step E, a compound of the invention, as a white solid melting at 72-74°C.

EXAMPLE 3

20 Step A: Methyl 2-[[[1,3-dihydro-1,3-dioxo-2H-isoindol-2-yl]oxy]methyl]-α-(methoxyimino)benzeneacetate

Triethylamine (2.8 mL) was added to a solution of 5 g of methyl 2-(bromomethyl)-α-(methoxyimino)benzeneacetate and 2.83 g of *N*-hydroxy-phthalimide in 12 mL of *N*-methylpyrrolidone. The reaction mixture was stirred at room temperature for 72 h and

25 then poured into 75 mL of ice water. The precipitate was removed by filtration and redissolved in methylene chloride. The organic phase was washed with 30 mL of water, dried (MgSO₄), filtered and concentrated *in vacuo* to yield 5.0 g (80% yield) of the title compound of Step A as a gray powder melting at 103-105°C. ¹H NMR (CDCl₃):

30 δ 7.8 (m,3H), 7.75 (m,2H), 7.50 (dt,J=1.5,7.5Hz,1H), 7.44 (dt,J=1.5,7.5Hz,1H)
7.17 (dd,J=1.5,7.5Hz,1H), 5.07 (s,2H), 3.97 (s,3H), 3.84 (s,3H).

Step B: 2-[(Aminooxy)methyl]-α-(methoxyimino)-*N*-methyl-benzeneacetamide

The title compound of Step A (5.0 g) was dissolved in 33 mL of 40% aqueous methylamine solution and heated to reflux for 4 hours. The solution was cooled and extracted with methylene chloride (3x30 mL) and the organic phase was washed with 30

35 mL of water. The organic phase was dried (MgSO₄), filtered and concentrated *in vacuo* to yield 5 g of a dark amber oil. Trituration in methyl *tert*-butyl ether/hexane provided 1.1 g (34% yield) of the title compound of Step B as an off-white solid melting at

91-93°C. ¹H NMR (CDCl₃): δ 7.4 (m, 3H), 7.15 (dd, J=2, 5.5 Hz, 1H), 6.8 (broad, 1H), 5.34 (br s, 2H), 4.59 (s, 2H), 3.94 (s, 3H), 2.93 (d, J=5 Hz, 3H).

Step C: α-(Methoxyimino)-N-methyl-2-[[[1-[3-

(trimethylsilyl)phenyl]ethylidene]amino]oxy]methyl]benzeneacetamide

- 5 A mixture of 430 mg of the title compound of Step B, 350 mg of 1-[3-(trimethylsilyl)phenyl]ethanone (Intermediate 1), and 100 mg of 3 Å molecular sieves in 3 mL of methanol was treated with ~20 mg of *p*-toluenesulfonic acid monohydrate at room temperature overnight. The mixture was filtered and the filtrate was concentrated *in vacuo* to yield an amber semisolid. The residue was purified by flash chromatography
- 10 (2:1 hexane:ethyl acetate as eluent). The first eluting component was collected to yield 540 mg (73% yield) of the title compound of Step C, a compound of the invention, as a colorless oil. ¹H NMR (CDCl₃): δ 7.7 (d, 1H), 7.53 (m, 3H), 7.37 (m, 3H), 7.20 (m, 1H), 6.7 (broad d, 1H), 5.13 (s, 2H), 3.94 (s, 3H), 2.83 (d, 3H), 2.21 (s, 3H), 0.27 (s, 9H).

EXAMPLE 4

- 15 Step A: 2-(4-Bromophenyl)-2-methyl-1,3-dioxolane

The compound, 1-(4-bromophenyl)ethanone (103 g, 0.52 mol), ethylene glycol (145 mL, 2.6 mol), and *p*-toluenesulfonic acid (0.2 g) were dissolved in benzene (350 mL) and heated at reflux overnight using a Dean-Stark apparatus. Water and some ethylene glycol had separated and the cooled (room temperature) mixture was poured

20 into water (550 mL) and extracted with diethyl ether (2x100 mL). The combined organic phases were dried (MgSO₄) and concentrated to give the crude product as a white solid. The solid was recrystallized (boiling pentane, followed by cooling in a dry ice/acetone bath) to give the title compound of Step A as white crystals melting at 38-40°C (126 g, 100% yield).

- 25 Step B: 1-[4-(Trimethylgermyl)phenyl]ethanone

A 1000 mL 4-neck flask was charged with a suspension of magnesium pieces (6.15 g, 0.253 mol) in 40 mL THF. A solution of the title compound of Step A (61.5 g, 0.253 mol) dissolved in 200 mL of THF was added dropwise; a few crystals of iodine were added to the mixture after a small portion of the solution had been added. Heating

30 to 49°C was required to initiate the reaction; the temperature was then maintained between 62-67°C during the remainder of the addition, at which time the mixture was heated at reflux for 2.5 h. After cooling the mixture to 50°C, a solution of trimethylgermanium bromide (50 g, 0.253 mol) dissolved in THF (50 mL) was added in small aliquots, allowing the exotherm from each addition to keep the temperature

35 between 65-67°C. The mixture was refluxed a total of 5.5 h, cooled, and poured into a saturated ammonium chloride solution (250 mL). Following separation of the organic layer and extraction with diethyl ether, the combined organic phases were dried (MgSO₄) and concentrated to give 63.3 g of a white solid. This solid was then dissolved

in acetone (500 mL) and 1 N HCl (14 mL) was added. The resulting solution was refluxed for 7 h. Concentration, followed by partitioning between water and diethyl ether, and finally drying (MgSO₄) the organic phase yielded 51.03 g (85% overall for both steps) of the title compound of Step B as a yellow oil. ¹H NMR (CDCl₃): δ 7.9 (d,2H), 7.5 (d,2H), 2.603 (s,3H), 0.414 (s,6H).

Step C: 1-[4-(Trimethylgermyl)phenyl]ethanone oxime

Sodium acetate trihydrate (29.2 g, 0.356 mol) was added to a solution of hydroxylamine hydrochloride (24.7 g, 0.356 mol) in water (160 mL), and this solution was added to a solution of the title compound of Step B (55.86 g, 0.236 mol) in methanol (320 mL). The mixture was then refluxed overnight and concentrated *in vacuo*. The mixture was treated with water and then extracted with methylene chloride (3x120 mL). The combined organic layers were washed with a saturated solution of sodium bicarbonate and then dried (MgSO₄) and concentrated to yield 58 g of a white solid. Boiling pentane and then cooling was used to recrystallize this solid to give the title compound of Step B as a white solid melting at 98-101°C (> 35g, > 59%).

Step D: Methyl α-(methoxymethylene)-2-[4-(trimethylgermyl)phenyl]ethylidenelaminoloxymethylbenzeneacetate

The title compound of Step C (0.13 g, 0.52 mmol) was dissolved in DMF (3 mL), treated with sodium hydride (0.02 g, 0.8 mmol) [60% mineral oil dispersion], and then stirred at room temperature for 30 min. Methyl 2-(bromomethyl)-α-(methoxymethylene)benzeneacetate (0.15 g, 0.52 mmol) was dissolved in DMF (3 mL) and added to the above solution. The mixture was stirred overnight, then poured into water (55 mL) and extracted with diethyl ether (5x50 mL) and once with ethyl acetate (50 mL). The combined organic phases were dried (MgSO₄), concentrated, and purified by flash chromatography (1:1 diethyl ether/hexanes as eluent) to yield the title compound of Step D, a compound of the invention, as a yellow oil (0.04 g, 20%). ¹H NMR (CDCl₃): δ 7.6 (d,2H), 7.5 (d,1H), 7.45 (d,3H), 7.3 (m,3H), 7.15 (d,1H), 5.15 (s,2H), 3.81 (s,3H), 3.68 (s,3H), 2.23 (s,3H), 0.38 s, 6.5H).

EXAMPLE 5

Step A: Methyl α-(methoxyimino)-2-[4-(trimethylsilyl)phenyl]ethylidenelaminoloxymethylbenzeneacetate

Intermediate 2 (0.37 g, 1.8 mmol) was dissolved in DMF (9 mL) and treated with sodium hydride (0.08 g, 3.3 mmol) [60% mineral oil dispersion] and stirred at room temperature for 30 min. Methyl 2-(bromomethyl)-α-(methoxyimino)benzeneacetate (0.52 g, 1.8 mmol) was dissolved in DMF (9 mL) and added to the above solution. The mixture was stirred overnight, and then poured into water (300 mL) and extracted once with ethyl acetate (50 mL) and then by diethyl ether (2x80 mL). The combined organic phases were dried (MgSO₄), concentrated, and purified by flash chromatography (30%

ethyl acetate/hexanes) to yield the title compound of Step A, a compound of the invention, as a yellow oil (0.48 g, 65%). ^1H NMR (CDCl_3): δ 7.7 (s,1H), 7.58 (d,1H), 7.55 (t,2H), 7.3-7.5 (m,3H), 7.2 (d,1H), 5.13 (s,2H), 4.03 (s,3H), 3.81 (s,3H), 2.21 (s,3H), 0.27 (s,7.4 H).

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EXAMPLE 6

Step A: (4-Bromo-2-methylphenoxy)(1,1-dimethylethyl)dimethylsilane

20.0 g of 4-bromo-2-methylphenol was dissolved in 80 mL of DMF and then sequentially treated with 19.6 g of *tert*-butyldimethylchlorosilane and 11.6 g of imidazole. After 3 hours, the reaction mixture was diluted with 300 mL of diethyl ether and washed with water (2x100 mL) and a saturated solution of CuSO_4 (2x100 mL). After drying (MgSO_4), the organic layer was concentrated under reduced pressure to yield a yellow oil which was vacuum distilled and the fraction collected from 95-98°C at 250 Pa provided 29.5 g of the title compound of Step A as an oil. ^1H NMR (CDCl_3): δ 7.25 (s,1H), 7.2 (d,1H), 6.6 (d,1H), 2.17 (s,3H), 1.01 (s,9H), 0.19 (s,6H).

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Step B: (1,1-Dimethylethyl)dimethyl[2-methyl-4-(trimethylgermyl)phenoxy]silane

0.49 g of magnesium pieces was suspended in 5 mL of THF containing one crystal of iodine. A solution of 6.03 g of the title compound of Step A dissolved in 12 mL of THF was added in small portions and the mixture was heated to 65°C until the reaction initiated, at which time the remaining solution was added dropwise at such a rate as to keep the temperature between 50-70°C. At the completion of the solution addition, the mixture was refluxed for 1.5 hours and then allowed to cool to 60°C. A solution of 2.6 mL of trimethylbromogermane dissolved in 5 mL THF was then added dropwise causing a large exotherm. The rate of addition was controlled to keep the temperature >65°C. At the end of the addition period, the mixture was refluxed for 4 h. After cooling to room temperature, the mixture was poured into 100 mL of 1N HCl. Following separation of the organic layer, the aqueous layer was extracted with diethyl ether (2x100 mL). The combined organic phases were dried (MgSO_4), filtered and concentrated under reduced pressure to yield 5.79 g of the title compound of Step B as a pink oil (90%). This material was used without further purification. ^1H NMR (CDCl_3): δ 7.2 (s,1H), 7.1 (d,1H), 6.77 (d,1H), 2.21 (s,3H), 1.0 (s,9H), 0.34 (s,8H), 0.22 (s,6H).

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Step C: 2-Methyl-4-(trimethylgermyl)phenol

1.74 g of the title compound of Step B was dissolved in 10 mL of THF and was treated dropwise with 7.0 mL of a 1.0 M solution of tetrabutylammonium fluoride in THF. The reaction solution immediately turned dark and was stirred overnight at room temperature. The mixture was partitioned between diethyl ether and water. Following separation of the organic layer, the aqueous phase was extracted twice with diethyl ether. The combined organic layers were dried (MgSO_4), filtered and concentrated under

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reduced pressure to yield a dark oil which was then filtered through a 5 cm plug of silica gel eluting with 5% ethyl acetate/hexanes to yield the title compound of Step C as an oil which was used without further purification. IR: 3321 cm^{-1} .

Step D: Methyl α -(methoxyimino)-2-[[2-methyl-4-(trimethylgermyl)phenoxy]methyl]benzeneacetate

The title compound of Step C was dissolved in 30 mL of 2-butanone. 0.5 g of finely ground (mortar and pestle) potassium carbonate was added followed by 0.5 g of methyl 2-(bromomethyl)- α -(methoxyimino)benzeneacetate and the resulting mixture was heated to reflux overnight. Evaporation of the solvent *in vacuo* was followed by partitioning between water and ethyl acetate. The resulting aqueous phase was extracted with ethyl acetate and diethyl ether. The combined organic layers were dried (MgSO_4), filtered and concentrated *in vacuo* to yield a dark oil which was purified by MPLC (20% ethyl acetate/hexanes) to give 0.32 g of the title compound of Step D, a compound of the invention. ^1H NMR (CDCl_3): δ 7.6 (d,1H), 7.3-7.5 (m,2H), 7.2 (m,2H), 6.8 (d,1H), 4.95 (s,2H), 4.02 (s,3H), 3.83 (s,3H), 2.25 (s,3H), 0.34 (s,7H).

Preparation of Intermediates 1 and 2

Step A: 2-(3-Bromophenyl)-2-methyl-1,3-dioxolane

The compound, 1-(3-bromophenyl)ethanone (35 g, 0.18 mol), ethylene glycol (39 mL, 0.70 mol), and *p*-toluenesulfonic acid (0.5 g) were dissolved in toluene (300 mL) and heated to reflux in a Dean-Stark apparatus. After six hours, water and some ethylene glycol had separated and the mixture was cooled and washed with water and saturated aqueous sodium bicarbonate solution. Drying (MgSO_4) and concentrating the organic phase gave the title compound of Step A as an oil (44 g, 99% yield). ^1H NMR (CDCl_3): δ 7.64 (m,1H), 7.39 (m,2H), 7.21 (t,1H), 4.04 (m,2H), 3.76 (m,2H), 1.63 (s,3H).

Step B: 1-[3-(Trimethylsilyl)phenyl]ethanone (Intermediate 1)

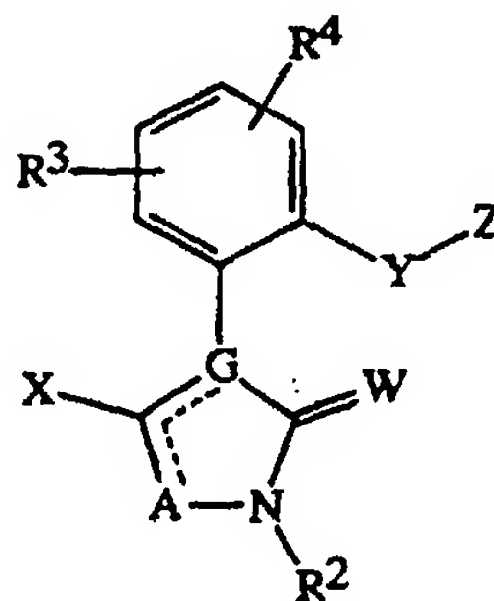
A flame-dried flask was charged with magnesium pieces (5.3 g, 0.22 mole) and tetrahydrofuran (50 mL) under a nitrogen atmosphere. To this vigorously stirred slurry was added dropwise the title compound of Step A (44 g, 0.18 mole) in THF (150 mL). The reaction mixture was warmed to 40°C during the addition and then to 65°C for 1.5 hours after the addition was complete. After cooling the solution to room temperature, trimethylsilyl chloride (28 mL, 0.22 mole) was added dropwise over 15 minutes and the reaction was allowed to stir for 16 hours. The reaction suspension was cooled to 10°C and treated with saturated aqueous ammonium chloride solution and extracted with diethyl ether. The combined organic phases were dried (MgSO_4) and concentrated to give the intermediate silylated ketal. This crude intermediate was dissolved in acetone (180 mL) and treated with 1N hydrochloric acid solution (18 mL) at reflux for 2 hours. After cooling, saturated aqueous sodium bicarbonate solution

(180 mL) was added carefully and the mixture extracted with methylene chloride. The combined organic phases were dried (MgSO_4) and concentrated to give the title compound of Step B (Intermediate 1) as a yellow oil (34 g, 99% yield). ^1H NMR (CDCl_3): δ 8.10 (s, 1H), 7.91 (m, 1H), 7.73 (m, 1H), 7.45 (t, 1H), 2.62 (s, 3H), 0.30 (s, 9H).

Step C: 1-[3-(Trimethylsilyl)phenyl]ethanone oxime (Intermediate 2)

Intermediate 1 (34 g, 0.18 mol) was dissolved in methanol (175 mL) and treated with a solution of hydroxylamine hydrochloride (19 g, 0.28 mol) and sodium acetate (38 g, 0.28 mol) in water (130 mL). The mixture was heated at reflux for 2.5 hours, cooled, and extracted with methylene chloride. The combined organic phases were dried (MgSO_4), concentrated, and chromatographed on silica gel with 10% ethyl acetate/hexane as eluent. The title compound of Step C (Intermediate 2) was isolated as a colorless oil (30 g, 80% yield). ^1H NMR (CDCl_3): δ 9.27 (s, 1H), 7.77 (s, 1H), 7.56 (m, 2H), 7.37 (t, 1H), 2.32 (s, 3H), 0.29 (s, 9H).

By the procedures described herein together with methods known in the art, the following compounds of Tables 1 to 79 can be prepared. The following abbreviations are used in the Tables which follow: *t* = tertiary, *n* = normal, *c* = cyclo, Me = methyl, Et = ethyl, Pr = propyl, Bu = butyl, Hex = hexyl, Ph = phenyl, MeO = methoxy, EtO = ethoxy, MeS = methylthio, EtS = ethylthio, CN = cyano, NO_2 = nitro, TMS = trimethylsilyl, and TBDMS = *t*-BuMe₂Si.



Formula I where E is E¹

Table 1

Compounds of Formula I wherein: E = E¹, G = C, W = O, R³ = R⁴ = H, Y = CH₂ON=C(CH₃), Z = 3-Me₃Si-Ph, the floating double bond is attached to G, and R² = Me

X	A	X	A	X	A	X	A
MeO	O	MeS	O	MeO	S	MeS	S
EtO	O	EtS	O	EtO	S	EtS	S

<i>n</i> -PrO	O	<i>n</i> -PrS	O	<i>n</i> -PrO	S	<i>n</i> -PrS	S
H ₂ C=CHCH ₂ O	O	H ₂ C=CHCH ₂ S	O	H ₂ C=CHCH ₂ O	S	H ₂ C=CHCH ₂ S	S
HC≡CCH ₂ O	O	HC≡CCH ₂ S	O	HC≡CCH ₂ O	S	HC≡CCH ₂ S	S
CF ₃ O	O	CF ₃ S	O	CF ₃ O	S	CF ₃ S	S
(<i>c</i> -propyl)O	O	Cl	O	(<i>c</i> -propyl)O	S	Cl	S

R² = Et

X	A	X	A	X	A	X	A
MeO	O	MeS	O	MeO	S	MeS	S
EtO	O	EtS	O	EtO	S	EtS	S
<i>n</i> -PrO	O	<i>n</i> -PrS	O	<i>n</i> -PrO	S	<i>n</i> -PrS	S
H ₂ C=CHCH ₂ O	O	H ₂ C=CHCH ₂ S	O	H ₂ C=CHCH ₂ O	S	H ₂ C=CHCH ₂ S	S
HC≡CCH ₂ O	O	HC≡CCH ₂ S	O	HC≡CCH ₂ O	S	HC≡CCH ₂ S	S
CF ₃ O	O	CF ₃ S	O	CF ₃ O	S	CF ₃ S	S
(<i>c</i> -propyl)O	O	Cl	O	(<i>c</i> -propyl)O	S	Cl	S

R² = *n*-Pr

X	A	X	A	X	A	X	A
MeO	O	MeS	O	MeO	S	MeS	S
EtO	O	EtS	O	EtO	S	EtS	S
<i>n</i> -PrO	O	<i>n</i> -PrS	O	<i>n</i> -PrO	S	<i>n</i> -PrS	S
H ₂ C=CHCH ₂ O	O	H ₂ C=CHCH ₂ S	O	H ₂ C=CHCH ₂ O	S	H ₂ C=CHCH ₂ S	S
HC≡CCH ₂ O	O	HC≡CCH ₂ S	O	HC≡CCH ₂ O	S	HC≡CCH ₂ S	S
CF ₃ O	O	CF ₃ S	O	CF ₃ O	S	CF ₃ S	S
(<i>c</i> -propyl)O	O	Cl	O	(<i>c</i> -propyl)O	S	Cl	S

R² = H

X	A	X	A	X	A	X	A
MeO	O	MeS	O	MeO	S	MeS	S
EtO	O	EtS	O	EtO	S	EtS	S
<i>n</i> -PrO	O	<i>n</i> -PrS	O	<i>n</i> -PrO	S	<i>n</i> -PrS	S
H ₂ C=CHCH ₂ O	O	H ₂ C=CHCH ₂ S	O	H ₂ C=CHCH ₂ O	S	H ₂ C=CHCH ₂ S	S
HC≡CCH ₂ O	O	HC≡CCH ₂ S	O	HC≡CCH ₂ O	S	HC≡CCH ₂ S	S
CF ₃ O	O	CF ₃ S	O	CF ₃ O	S	CF ₃ S	S
(<i>c</i> -propyl)O	O	Cl	O	(<i>c</i> -propyl)O	S	Cl	S

R² = Me

X	A	X	A	X	A	X	A
MeO	NH	MeS	NH	MeO	NMe	MeS	NMe

EtO	NH	EtS	NH	EtO	NMe	EtS	NMe
<i>n</i> -PrO	NH	<i>n</i> -PrS	NH	<i>n</i> -PrO	NMe	<i>n</i> -PrS	NMe
H ₂ C=CHCH ₂ O	NH	H ₂ C=CHCH ₂ S	NH	H ₂ C=CHCH ₂ O	NMe	H ₂ C=CHCH ₂ S	NMe
HC≡CCH ₂ O	NH	HC≡CCH ₂ S	NH	HC≡CCH ₂ O	NMe	HC≡CCH ₂ S	NMe
CF ₃ O	NH	CF ₃ S	NH	CF ₃ O	NMe	CF ₃ S	NMe
(<i>c</i> -propyl)O	NH	Cl	NH	(<i>c</i> -propyl)O	NMe	Cl	NMe

 $R^2 = H$

X	A	X	A	X	A	X	A
MeO	NH	MeS	NH	MeO	NMe	MeS	NMe
EtO	NH	EtS	NH	EtO	NMe	EtS	NMe
<i>n</i> -PrO	NH	<i>n</i> -PrS	NH	<i>n</i> -PrO	NMe	<i>n</i> -PrS	NMe
H ₂ C=CHCH ₂ O	NH	H ₂ C=CHCH ₂ S	NH	H ₂ C=CHCH ₂ O	NMe	H ₂ C=CHCH ₂ S	NMe
HC≡CCH ₂ O	NH	HC≡CCH ₂ S	NH	HC≡CCH ₂ O	NMe	HC≡CCH ₂ S	NMe
CF ₃ O	NH	CF ₃ S	NH	CF ₃ O	NMe	CF ₃ S	NMe
(<i>c</i> -propyl)O	NH	Cl	NH	(<i>c</i> -propyl)O	NMe	Cl	NMe

Table 2

Compounds of Formula I wherein: E = E¹, G = N, W = O, R³ = R⁴ = H, Y = CH₂ON=C(CH₃).Z = 3-Me₃Si-Ph, the floating double bond is attached to A, and $R^2 = Me$

X	A	X	A	X	A	X	A
MeO	N	MeS	N	MeO	CH	MeS	CH
EtO	N	EtS	N	EtO	CH	EtS	CH
<i>n</i> -PrO	N	<i>n</i> -PrS	N	<i>n</i> -PrO	CH	<i>n</i> -PrS	CH
H ₂ C=CHCH ₂ O	N	H ₂ C=CHCH ₂ S	N	H ₂ C=CHCH ₂ O	CH	H ₂ C=CHCH ₂ S	CH
HC≡CCH ₂ O	N	HC≡CCH ₂ S	N	HC≡CCH ₂ O	CH	HC≡CCH ₂ S	CH
CF ₃ O	N	CF ₃ S	N	CF ₃ O	CH	CF ₃ S	CH
(<i>c</i> -propyl)O	N	Cl	N	(<i>c</i> -propyl)O	CH	Cl	CH

 $R^2 = Et$

X	A	X	A	X	A	X	A
MeO	N	MeS	N	MeO	CH	MeS	CH
EtO	N	EtS	N	EtO	CH	EtS	CH
<i>n</i> -PrO	N	<i>n</i> -PrS	N	<i>n</i> -PrO	CH	<i>n</i> -PrS	CH
H ₂ C=CHCH ₂ O	N	H ₂ C=CHCH ₂ S	N	H ₂ C=CHCH ₂ O	CH	H ₂ C=CHCH ₂ S	CH
HC≡CCH ₂ O	N	HC≡CCH ₂ S	N	HC≡CCH ₂ O	CH	HC≡CCH ₂ S	CH
CF ₃ O	N	CF ₃ S	N	CF ₃ O	CH	CF ₃ S	CH

(c-propyl)O	N	Cl	N	(c-propyl)O	CH	Cl	CH
$R^2 = n\text{-Pr}$							
X	A	X	A	X	A	X	A
MeO	N	MeS	N	MeO	CH	MeS	CH
EtO	N	EtS	N	EtO	CH	EtS	CH
n-PrO	N	n-PrS	N	n-PrO	CH	n-PrS	CH
H ₂ C=CHCH ₂ O	N	H ₂ C=CHCH ₂ S	N	H ₂ C=CHCH ₂ O	CH	H ₂ C=CHCH ₂ S	CH
HC≡CCH ₂ O	N	HC≡CCH ₂ S	N	HC≡CCH ₂ O	CH	HC≡CCH ₂ S	CH
CF ₃ O	N	CF ₃ S	N	CF ₃ O	CH	CF ₃ S	CH
(c-propyl)O	N	Cl	N	(c-propyl)O	CH	Cl	CH

$R^2 = H$							
X	A	X	A	X	A	X	A
MeO	N	MeS	N	MeO	CH	MeS	CH
EtO	N	EtS	N	EtO	CH	EtS	CH
n-PrO	N	n-PrS	N	n-PrO	CH	n-PrS	CH
H ₂ C=CHCH ₂ O	N	H ₂ C=CHCH ₂ S	N	H ₂ C=CHCH ₂ O	CH	H ₂ C=CHCH ₂ S	CH
HC≡CCH ₂ O	N	HC≡CCH ₂ S	N	HC≡CCH ₂ O	CH	HC≡CCH ₂ S	CH
CF ₃ O	N	CF ₃ S	N	CF ₃ O	CH	CF ₃ S	CH
(c-propyl)O	N	Cl	N	(c-propyl)O	CH	Cl	CH

$R^2 = Me$							
X	A	X	A	X	A	X	A
MeO	CMe	MeS	CMe	MeO	CEt	MeS	CEt
EtO	CMe	EtS	CMe	EtO	CEt	EtS	CEt
n-PrO	CMe	n-PrS	CMe	n-PrO	CEt	n-PrS	CEt
H ₂ C=CHCH ₂ O	CMe	H ₂ C=CHCH ₂ S	CMe	H ₂ C=CHCH ₂ O	CEt	H ₂ C=CHCH ₂ S	CEt
HC≡CCH ₂ O	CMe	HC≡CCH ₂ S	CMe	HC≡CCH ₂ O	CEt	HC≡CCH ₂ S	CEt
CF ₃ O	CMe	CF ₃ S	CMe	CF ₃ O	CEt	CF ₃ S	CEt
(c-propyl)O	CMe	Cl	CMe	(c-propyl)O	CEt	Cl	CEt

$R^2 = H$							
X	A	X	A	X	A	X	A
MeO	CEt	MeS	CEt	MeO	CMe	MeS	CMe
EtO	CEt	EtS	CEt	EtO	CMe	EtS	CMe
n-PrO	CEt	n-PrS	CEt	n-PrO	CMe	n-PrS	CMe
H ₂ C=CHCH ₂ O	CEt	H ₂ C=CHCH ₂ S	CEt	H ₂ C=CHCH ₂ O	CMe	H ₂ C=CHCH ₂ S	CMe

HC≡CCH ₂ O	CEt	HC≡CCH ₂ S	CEt	HC≡CCH ₂ O	CMe	HC≡CCH ₂ S	CMe
CF ₃ O	CEt	CF ₃ S	CEt	CF ₃ O	CMe	CF ₃ S	CMe
(<i>c</i> -propyl)O	CEt	Cl	CEt	(<i>c</i> -propyl)O	CMe	Cl	CMe

Table 3

Compounds of Formula I wherein: E = E¹, G = C, W = O, R³ = R⁴ = H,

Y = CH₂ON=C(CH₃), Z = 4-Me₃Si-Ph, the floating double bond is attached to G, and

R² = Me

X	A	X	A	X	A	X	A
MeO	O	MeS	O	MeO	S	MeS	S
EtO	O	EtS	O	EtO	S	EtS	S
<i>n</i> -PrO	O	<i>n</i> -PrS	O	<i>n</i> -PrO	S	<i>n</i> -PrS	S
H ₂ C=CHCH ₂ O	O	H ₂ C=CHCH ₂ S	O	H ₂ C=CHCH ₂ O	S	H ₂ C=CHCH ₂ S	S
HC≡CCH ₂ O	O	HC≡CCH ₂ S	O	HC≡CCH ₂ O	S	HC≡CCH ₂ S	S
CF ₃ O	O	CF ₃ S	O	CF ₃ O	S	CF ₃ S	S
(<i>c</i> -propyl)O	O	Cl	O	(<i>c</i> -propyl)O	S	Cl	S

R² = Et

X	A	X	A	X	A	X	A
MeO	O	MeS	O	MeO	S	MeS	S
EtO	O	EtS	O	EtO	S	EtS	S
<i>n</i> -PrO	O	<i>n</i> -PrS	O	<i>n</i> -PrO	S	<i>n</i> -PrS	S
H ₂ C=CHCH ₂ O	O	H ₂ C=CHCH ₂ S	O	H ₂ C=CHCH ₂ O	S	H ₂ C=CHCH ₂ S	S
HC≡CCH ₂ O	O	HC≡CCH ₂ S	O	HC≡CCH ₂ O	S	HC≡CCH ₂ S	S
CF ₃ O	O	CF ₃ S	O	CF ₃ O	S	CF ₃ S	S
(<i>c</i> -propyl)O	O	Cl	O	(<i>c</i> -propyl)O	S	Cl	S

R² = *n*-Pr

X	A	X	A	X	A	X	A
MeO	O	MeS	O	MeO	S	MeS	S
EtO	O	EtS	O	EtO	S	EtS	S
<i>n</i> -PrO	O	<i>n</i> -PrS	O	<i>n</i> -PrO	S	<i>n</i> -PrS	S
H ₂ C=CHCH ₂ O	O	H ₂ C=CHCH ₂ S	O	H ₂ C=CHCH ₂ O	S	H ₂ C=CHCH ₂ S	S
HC≡CCH ₂ O	O	HC≡CCH ₂ S	O	HC≡CCH ₂ O	S	HC≡CCH ₂ S	S
CF ₃ O	O	CF ₃ S	O	CF ₃ O	S	CF ₃ S	S
(<i>c</i> -propyl)O	O	Cl	O	(<i>c</i> -propyl)O	S	Cl	S

$R^2 = H$

X	A	X	A	X	A	X	A
MeO	O	MeS	O	MeO	S	MeS	S
EtO	O	EtS	O	EtO	S	EtS	S
<i>n</i> -PrO	O	<i>n</i> -PrS	O	<i>n</i> -PrO	S	<i>n</i> -PrS	S
H ₂ C=CHCH ₂ O	O	H ₂ C=CHCH ₂ S	O	H ₂ C=CHCH ₂ O	S	H ₂ C=CHCH ₂ S	S
HC≡CCH ₂ O	O	HC≡CCH ₂ S	O	HC≡CCH ₂ O	S	HC≡CCH ₂ S	S
CF ₃ O	O	CF ₃ S	O	CF ₃ O	S	CF ₃ S	S
(<i>c</i> -propyl)O	O	Cl	O	(<i>c</i> -propyl)O	S	Cl	S

 $R^2 = Me$

X	A	X	A	X	A	X	A
MeO	NH	MeS	NH	MeO	NMe	MeS	NMe
EtO	NH	EtS	NH	EtO	NMe	EtS	NMe
<i>n</i> -PrO	NH	<i>n</i> -PrS	NH	<i>n</i> -PrO	NMe	<i>n</i> -PrS	NMe
H ₂ C=CHCH ₂ O	NH	H ₂ C=CHCH ₂ S	NH	H ₂ C=CHCH ₂ O	NMe	H ₂ C=CHCH ₂ S	NMe
HC≡CCH ₂ O	NH	HC≡CCH ₂ S	NH	HC≡CCH ₂ O	NMe	HC≡CCH ₂ S	NMe
CF ₃ O	NH	CF ₃ S	NH	CF ₃ O	NMe	CF ₃ S	NMe
(<i>c</i> -propyl)O	NH	Cl	NH	(<i>c</i> -propyl)O	NMe	Cl	NMe

 $R^2 = H$

X	A	X	A	X	A	X	A
MeO	NH	MeS	NH	MeO	NMe	MeS	NMe
EtO	NH	EtS	NH	EtO	NMe	EtS	NMe
<i>n</i> -PrO	NH	<i>n</i> -PrS	NH	<i>n</i> -PrO	NMe	<i>n</i> -PrS	NMe
H ₂ C=CHCH ₂ O	NH	H ₂ C=CHCH ₂ S	NH	H ₂ C=CHCH ₂ O	NMe	H ₂ C=CHCH ₂ S	NMe
HC≡CCH ₂ O	NH	Cl	NH	HC≡CCH ₂ O	NMe	Cl	NMe
CF ₃ O	NH	CF ₃ S	NH	CF ₃ O	NMe	CF ₃ S	NMe
(<i>c</i> -propyl)O	NH	Cl	NH	(<i>c</i> -propyl)O	NMe	Cl	NMe

Table 4

Compounds of Formula I wherein: $E = E^1$, $G = N$, $W = O$, $R^3 = R^4 = H$, $Y = CH_2ON=C(CH_3)$,
 $Z = 4-Me_3Si-Ph$, the floating double bond is attached to A, and

 $R^2 = Me$

X	A	X	A	X	A	X	A
MeO	N	MeS	N	MeO	CH	MeS	CH
EtO	N	EtS	N	EtO	CH	EtS	CH
<i>n</i> -PrO	N	<i>n</i> -PrS	N	<i>n</i> -PrO	CH	<i>n</i> -PrS	CH

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$\text{H}_2\text{C}=\text{CHCH}_2\text{O}$	N	$\text{H}_2\text{C}=\text{CHCH}_2\text{S}$	N	$\text{H}_2\text{C}=\text{CHCH}_2\text{O}$	CH	$\text{H}_2\text{C}=\text{CHCH}_2\text{S}$	CH
$\text{HC}\equiv\text{CCH}_2\text{O}$	N	$\text{HC}\equiv\text{CCH}_2\text{S}$	N	$\text{HC}\equiv\text{CCH}_2\text{O}$	CH	$\text{HC}\equiv\text{CCH}_2\text{S}$	CH
CF_3O	N	CF_3S	N	CF_3O	CH	CF_3S	CH
$(c\text{-propyl})\text{O}$	N	Cl	N	$(c\text{-propyl})\text{O}$	CH	Cl	CH

 $\text{R}^2 = \text{Et}$

X	A	X	A	X	A	X	A
MeO	N	MeS	N	MeO	CH	MeS	CH
EtO	N	EtS	N	EtO	CH	EtS	CH
<i>n</i> -PrO	N	<i>n</i> -PrS	N	<i>n</i> -PrO	CH	<i>n</i> -PrS	CH
$\text{H}_2\text{C}=\text{CHCH}_2\text{O}$	N	$\text{H}_2\text{C}=\text{CHCH}_2\text{S}$	N	$\text{H}_2\text{C}=\text{CHCH}_2\text{O}$	CH	$\text{H}_2\text{C}=\text{CHCH}_2\text{S}$	CH
$\text{HC}\equiv\text{CCH}_2\text{O}$	N	$\text{HC}\equiv\text{CCH}_2\text{S}$	N	$\text{HC}\equiv\text{CCH}_2\text{O}$	CH	$\text{HC}\equiv\text{CCH}_2\text{S}$	CH
CF_3O	N	CF_3S	N	CF_3O	CH	CF_3S	CH
$(c\text{-propyl})\text{O}$	N	Cl	N	$(c\text{-propyl})\text{O}$	CH	Cl	CH

 $\text{R}^2 = n\text{-Pr}$

X	A	X	A	X	A	X	A
MeO	N	MeS	N	MeO	CH	MeS	CH
EtO	N	EtS	N	EtO	CH	EtS	CH
<i>n</i> -PrO	N	<i>n</i> -PrS	N	<i>n</i> -PrO	CH	<i>n</i> -PrS	CH
$\text{H}_2\text{C}=\text{CHCH}_2\text{O}$	N	$\text{H}_2\text{C}=\text{CHCH}_2\text{S}$	N	$\text{H}_2\text{C}=\text{CHCH}_2\text{O}$	CH	$\text{H}_2\text{C}=\text{CHCH}_2\text{S}$	CH
$\text{HC}\equiv\text{CCH}_2\text{O}$	N	$\text{HC}\equiv\text{CCH}_2\text{S}$	N	$\text{HC}\equiv\text{CCH}_2\text{O}$	CH	$\text{HC}\equiv\text{CCH}_2\text{S}$	CH
CF_3O	N	CF_3S	N	CF_3O	CH	CF_3S	CH
$(c\text{-propyl})\text{O}$	N	Cl	N	$(c\text{-propyl})\text{O}$	CH	Cl	CH

 $\text{R}^2 = \text{H}$

X	A	X	A	X	A	X	A
MeO	N	MeS	N	MeO	CH	MeS	CH
EtO	N	EtS	N	EtO	CH	EtS	CH
<i>n</i> -PrO	N	<i>n</i> -PrS	N	<i>n</i> -PrO	CH	<i>n</i> -PrS	CH
$\text{H}_2\text{C}=\text{CHCH}_2\text{O}$	N	$\text{H}_2\text{C}=\text{CHCH}_2\text{S}$	N	$\text{H}_2\text{C}=\text{CHCH}_2\text{O}$	CH	$\text{H}_2\text{C}=\text{CHCH}_2\text{S}$	CH
$\text{HC}\equiv\text{CCH}_2\text{O}$	N	$\text{HC}\equiv\text{CCH}_2\text{S}$	N	$\text{HC}\equiv\text{CCH}_2\text{O}$	CH	$\text{HC}\equiv\text{CCH}_2\text{S}$	CH
CF_3O	N	CF_3S	N	CF_3O	CH	CF_3S	CH
$(c\text{-propyl})\text{O}$	N	Cl	N	$(c\text{-propyl})\text{O}$	CH	Cl	CH

 $\text{R}^2 = \text{Me}$

X	A	X	A	X	A	X	A
MeO	CMe	MeS	CMe	MeO	CEt	MeS	CEt

EtO	CMe	EtS	CMe	EtO	CEt	EtS	CEt
<i>n</i> -PrO	CMe	<i>n</i> -PrS	CMe	<i>n</i> -PrO	CEt	<i>n</i> -PrS	CEt
H ₂ C=CHCH ₂ O	CMe	H ₂ C=CHCH ₂ S	CMe	H ₂ C=CHCH ₂ O	CEt	H ₂ C=CHCH ₂ S	CEt
HC≡CCH ₂ O	CMe	HC≡CCH ₂ S	CMe	HC≡CCH ₂ O	CEt	HC≡CCH ₂ S	CEt
CF ₃ O	CMe	CF ₃ S	CMe	CF ₃ O	CEt	CF ₃ S	CEt
(<i>c</i> -propyl)O	CMe	Cl	CMe	(<i>c</i> -propyl)O	CEt	Cl	CEt

 $R^2 = H$

\underline{X}	\underline{A}	\underline{X}	\underline{A}	\underline{X}	\underline{A}	\underline{X}	\underline{A}
MeO	CEt	MeS	CEt	MeO	CMe	MeS	CMe
EtO	CEt	EtS	CEt	EtO	CMe	EtS	CMe
<i>n</i> -PrO	CEt	<i>n</i> -PrS	CEt	<i>n</i> -PrO	CMe	<i>n</i> -PrS	CMe
H ₂ C=CHCH ₂ O	CEt	H ₂ C=CHCH ₂ S	CEt	H ₂ C=CHCH ₂ O	CMe	H ₂ C=CHCH ₂ S	CMe
HC≡CCH ₂ O	CEt	HC≡CCH ₂ S	CEt	HC≡CCH ₂ O	CMe	HC≡CCH ₂ S	CMe
CF ₃ O	CEt	CF ₃ S	CEt	CF ₃ O	CMe	CF ₃ S	CMe
(<i>c</i> -propyl)O	CEt	Cl	CEt	(<i>c</i> -propyl)O	CMe	Cl	CMe

Table 5

Compounds of Formula I wherein: $E = E^1$, $G = C$, $W = O$, $R^3 = R^4 = H$, $Y = CH_2ON=C(CH_3)$,
 $Z = 3\text{-Me}_3\text{Ge-Ph}$, the floating double bond is attached to G, and

 $R^2 = Me$

\underline{X}	\underline{A}	\underline{X}	\underline{A}	\underline{X}	\underline{A}	\underline{X}	\underline{A}
MeO	O	MeS	O	MeO	S	MeS	S
EtO	O	EtS	O	EtO	S	EtS	S
<i>n</i> -PrO	O	<i>n</i> -PrS	O	<i>n</i> -PrO	S	<i>n</i> -PrS	S
H ₂ C=CHCH ₂ O	O	H ₂ C=CHCH ₂ S	O	H ₂ C=CHCH ₂ O	S	H ₂ C=CHCH ₂ S	S
HC≡CCH ₂ O	O	HC≡CCH ₂ S	O	HC≡CCH ₂ O	S	HC≡CCH ₂ S	S
CF ₃ O	O	CF ₃ S	O	CF ₃ O	S	CF ₃ S	S
(<i>c</i> -propyl)O	O	Cl	O	(<i>c</i> -propyl)O	S	Cl	S

 $R^2 = Et$

\underline{X}	\underline{A}	\underline{X}	\underline{A}	\underline{X}	\underline{A}	\underline{X}	\underline{A}
MeO	O	MeS	O	MeO	S	MeS	S
EtO	O	EtS	O	EtO	S	EtS	S
<i>n</i> -PrO	O	<i>n</i> -PrS	O	<i>n</i> -PrO	S	<i>n</i> -PrS	S
H ₂ C=CHCH ₂ O	O	H ₂ C=CHCH ₂ S	O	H ₂ C=CHCH ₂ O	S	H ₂ C=CHCH ₂ S	S
HC≡CCH ₂ O	O	HC≡CCH ₂ S	O	HC≡CCH ₂ O	S	HC≡CCH ₂ S	S
CF ₃ O	O	CF ₃ S	O	CF ₃ O	S	CF ₃ S	S

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(c-propyl)O

O | Cl

O | (c-propyl)O

S | Cl

S |

 $R^2 = n\text{-Pr}$

X	A	X	A	X	A	X	A
MeO	O	MeS	O	MeO	S	MeS	S
EtO	O	EtS	O	EtO	S	EtS	S
n-PrO	O	n-PrS	O	n-PrO	S	n-PrS	S
H ₂ C=CHCH ₂ O	O	H ₂ C=CHCH ₂ S	O	H ₂ C=CHCH ₂ O	S	H ₂ C=CHCH ₂ S	S
HC≡CCH ₂ O	O	HC≡CCH ₂ S	O	HC≡CCH ₂ O	S	HC≡CCH ₂ S	S
CF ₃ O	O	CF ₃ S	O	CF ₃ O	S	CF ₃ S	S
(c-propyl)O	O	Cl	O	(c-propyl)O	S	Cl	S

 $R^2 = H$

X	A	X	A	X	A	X	A
MeO	O	MeS	O	MeO	S	MeS	S
EtO	O	EtS	O	EtO	S	EtS	S
n-PrO	O	n-PrS	O	n-PrO	S	n-PrS	S
H ₂ C=CHCH ₂ O	O	H ₂ C=CHCH ₂ S	O	H ₂ C=CHCH ₂ O	S	H ₂ C=CHCH ₂ S	S
HC≡CCH ₂ O	O	HC≡CCH ₂ S	O	HC≡CCH ₂ O	S	HC≡CCH ₂ S	S
CF ₃ O	O	CF ₃ S	O	CF ₃ O	S	CF ₃ S	S
(c-propyl)O	O	Cl	O	(c-propyl)O	S	Cl	S

 $R^2 = Me$

X	A	X	A	X	A	X	A
MeO	NH	MeS	NH	MeO	NMe	MeS	NMe
EtO	NH	EtS	NH	EtO	NMe	EtS	NMe
n-PrO	NH	n-PrS	NH	n-PrO	NMe	n-PrS	NMe
H ₂ C=CHCH ₂ O	NH	H ₂ C=CHCH ₂ S	NH	H ₂ C=CHCH ₂ O	NMe	H ₂ C=CHCH ₂ S	NMe
HC≡CCH ₂ O	NH	HC≡CCH ₂ S	NH	HC≡CCH ₂ O	NMe	HC≡CCH ₂ S	NMe
CF ₃ O	NH	CF ₃ S	NH	CF ₃ O	NMe	CF ₃ S	NMe
(c-propyl)O	NH	Cl	NH	(c-propyl)O	NMe	Cl	NMe

 $R^2 = H$

X	A	X	A	X	A	X	A
MeO	NH	MeS	NH	MeO	NMe	MeS	NMe
EtO	NH	EtS	NH	EtO	NMe	EtS	NMe
n-PrO	NH	n-PrS	NH	n-PrO	NMe	n-PrS	NMe
H ₂ C=CHCH ₂ O	NH	H ₂ C=CHCH ₂ S	NH	H ₂ C=CHCH ₂ O	NMe	H ₂ C=CHCH ₂ S	NMe

HC≡CCH ₂ O	NH	HC≡CCH ₂ S	NH	HC≡CCH ₂ O	NMe	HC≡CCH ₂ S	NMe
CF ₃ O	NH	CF ₃ S	NH	CF ₃ O	NMe	CF ₃ S	NMe
(<i>c</i> -propyl)O	NH	Cl	NH	(<i>c</i> -propyl)O	NMe	Cl	NMe

Table 6

Compounds of Formula I wherein: E = E¹, G = N, W = O, R³ = R⁴ = H, Y = CH₂ON=C(CH₃),
Z = 3-Me₃Ge-Ph, the floating double bond is attached to A, and

R² = Me

X	A	X	A	X	A	X	A
MeO	N	MeS	N	MeO	CH	MeS	CH
EtO	N	EtS	N	EtO	CH	EtS	CH
<i>n</i> -PrO	N	<i>n</i> -PrS	N	<i>n</i> -PrO	CH	<i>n</i> -PrS	CH
H ₂ C=CHCH ₂ O	N	H ₂ C=CHCH ₂ S	N	H ₂ C=CHCH ₂ O	CH	H ₂ C=CHCH ₂ S	CH
HC≡CCH ₂ O	N	HC≡CCH ₂ S	N	HC≡CCH ₂ O	CH	HC≡CCH ₂ S	CH
CF ₃ O	N	CF ₃ S	N	CF ₃ O	CH	CF ₃ S	CH
(<i>c</i> -propyl)O	N	Cl	N	(<i>c</i> -propyl)O	CH	Cl	CH

R² = Et

X	A	X	A	X	A	X	A
MeO	N	MeS	N	MeO	CH	MeS	CH
EtO	N	EtS	N	EtO	CH	EtS	CH
<i>n</i> -PrO	N	<i>n</i> -PrS	N	<i>n</i> -PrO	CH	<i>n</i> -PrS	CH
H ₂ C=CHCH ₂ O	N	H ₂ C=CHCH ₂ S	N	H ₂ C=CHCH ₂ O	CH	H ₂ C=CHCH ₂ S	CH
HC≡CCH ₂ O	N	HC≡CCH ₂ S	N	HC≡CCH ₂ O	CH	HC≡CCH ₂ S	CH
CF ₃ O	N	CF ₃ S	N	CF ₃ O	CH	CF ₃ S	CH
(<i>c</i> -propyl)O	N	Cl	N	(<i>c</i> -propyl)O	CH	Cl	CH

R² = *n*-Pr

X	A	X	A	X	A	X	A
MeO	N	MeS	N	MeO	CH	MeS	CH
EtO	N	EtS	N	EtO	CH	EtS	CH
<i>n</i> -PrO	N	<i>n</i> -PrS	N	<i>n</i> -PrO	CH	<i>n</i> -PrS	CH
H ₂ C=CHCH ₂ O	N	H ₂ C=CHCH ₂ S	N	H ₂ C=CHCH ₂ O	CH	H ₂ C=CHCH ₂ S	CH
HC≡CCH ₂ O	N	HC≡CCH ₂ S	N	HC≡CCH ₂ O	CH	HC≡CCH ₂ S	CH
CF ₃ O	N	CF ₃ S	N	CF ₃ O	CH	CF ₃ S	CH
(<i>c</i> -propyl)O	N	Cl	N	(<i>c</i> -propyl)O	CH	Cl	CH

$R^2 = H$

X	A	X	A	X	A	X	A
MeO	N	MeS	N	MeO	CH	MeS	CH
EtO	N	EtS	N	EtO	CH	EtS	CH
<i>n</i> -PrO	N	<i>n</i> -PrS	N	<i>n</i> -PrO	CH	<i>n</i> -PrS	CH
H ₂ C=CHCH ₂ O	N	H ₂ C=CHCH ₂ S	N	H ₂ C=CHCH ₂ O	CH	H ₂ C=CHCH ₂ S	CH
HC≡CCH ₂ O	N	HC≡CCH ₂ S	N	HC≡CCH ₂ O	CH	HC≡CCH ₂ S	CH
CF ₃ O	N	CF ₃ S	N	CF ₃ O	CH	CF ₃ S	CH
(<i>c</i> -propyl)O	N	Cl	N	(<i>c</i> -propyl)O	CH	Cl	CH

 $R^2 = Me$

X	A	X	A	X	A	X	A
MeO	CMe	MeS	CMe	MeO	CEt	MeS	CEt
EtO	CMe	EtS	CMe	EtO	CEt	EtS	CEt
<i>n</i> -PrO	CMe	<i>n</i> -PrS	CMe	<i>n</i> -PrO	CEt	<i>n</i> -PrS	CEt
H ₂ C=CHCH ₂ O	CMe	H ₂ C=CHCH ₂ S	CMe	H ₂ C=CHCH ₂ O	CEt	H ₂ C=CHCH ₂ S	CEt
HC≡CCH ₂ O	CMe	HC≡CCH ₂ S	CMe	HC≡CCH ₂ O	CEt	HC≡CCH ₂ S	CEt
CF ₃ O	CMe	CF ₃ S	CMe	CF ₃ O	CEt	CF ₃ S	CEt
(<i>c</i> -propyl)O	CMe	Cl	CMe	(<i>c</i> -propyl)O	CEt	Cl	CEt

 $R^2 = H$

X	A	X	A	X	A	X	A
MeO	CEt	MeS	CEt	MeO	CMe	MeS	CMe
EtO	CEt	EtS	CEt	EtO	CMe	EtS	CMe
<i>n</i> -PrO	CEt	<i>n</i> -PrS	CEt	<i>n</i> -PrO	CMe	<i>n</i> -PrS	CMe
H ₂ C=CHCH ₂ O	CEt	H ₂ C=CHCH ₂ S	CEt	H ₂ C=CHCH ₂ O	CMe	H ₂ C=CHCH ₂ S	CMe
HC≡CCH ₂ O	CEt	HC≡CCH ₂ S	CEt	HC≡CCH ₂ O	CMe	HC≡CCH ₂ S	CMe
CF ₃ O	CEt	CF ₃ S	CEt	CF ₃ O	CMe	CF ₃ S	CMe
(<i>c</i> -propyl)O	CEt	Cl	CEt	(<i>c</i> -propyl)O	CMe	Cl	CMe

Table 7

Compounds of Formula I wherein: E = E¹, G = C, W = O, R³ = R⁴ = H, Y = CH₂ON=C(CH₃),
Z = 4-Me₃Ge-Ph, the floating double bond is attached to G, and

 $R^2 = Me$

X	A	X	A	X	A	X	A
MeO	O	MeS	O	MeO	S	MeS	S
EtO	O	EtS	O	EtO	S	EtS	S
<i>n</i> -PrO	O	<i>n</i> -PrS	O	<i>n</i> -PrO	S	<i>n</i> -PrS	S

H ₂ C=CHCH ₂ O	O	H ₂ C=CHCH ₂ S	O	H ₂ C=CHCH ₂ O	S	H ₂ C=CHCH ₂ S	S
HC≡CCH ₂ O	O	HC≡CCH ₂ S	O	HC≡CCH ₂ O	S	HC≡CCH ₂ S	S
CF ₃ O	O	CF ₃ S	O	CF ₃ O	S	CF ₃ S	S
(<i>c</i> -propyl)O	O	Cl	O	(<i>c</i> -propyl)O	S	Cl	S

 $R^2 = Et$

X	A	X	A	X	A	X	A
MeO	O	MeS	O	MeO	S	MeS	S
EtO	O	EtS	O	EtO	S	EtS	S
<i>n</i> -PrO	O	<i>n</i> -PrS	O	<i>n</i> -PrO	S	<i>n</i> -PrS	S
H ₂ C=CHCH ₂ O	O	H ₂ C=CHCH ₂ S	O	H ₂ C=CHCH ₂ O	S	H ₂ C=CHCH ₂ S	S
HC≡CCH ₂ O	O	HC≡CCH ₂ S	O	HC≡CCH ₂ O	S	HC≡CCH ₂ S	S
CF ₃ O	O	CF ₃ S	O	CF ₃ O	S	CF ₃ S	S
(<i>c</i> -propyl)O	O	Cl	O	(<i>c</i> -propyl)O	S	Cl	S

 $R^2 = n-Pr$

X	A	X	A	X	A	X	A
MeO	O	MeS	O	MeO	S	MeS	S
EtO	O	EtS	O	EtO	S	EtS	S
<i>n</i> -PrO	O	<i>n</i> -PrS	O	<i>n</i> -PrO	S	<i>n</i> -PrS	S
H ₂ C=CHCH ₂ O	O	H ₂ C=CHCH ₂ S	O	H ₂ C=CHCH ₂ O	S	H ₂ C=CHCH ₂ S	S
HC≡CCH ₂ O	O	HC≡CCH ₂ S	O	HC≡CCH ₂ O	S	HC≡CCH ₂ S	S
CF ₃ O	O	CF ₃ S	O	CF ₃ O	S	CF ₃ S	S
(<i>c</i> -propyl)O	O	Cl	O	(<i>c</i> -propyl)O	S	Cl	S

 $R^2 = H$

X	A	X	A	X	A	X	A
MeO	O	MeS	O	MeO	S	MeS	S
EtO	O	EtS	O	EtO	S	EtS	S
<i>n</i> -PrO	O	<i>n</i> -PrS	O	<i>n</i> -PrO	S	<i>n</i> -PrS	S
H ₂ C=CHCH ₂ O	O	H ₂ C=CHCH ₂ S	O	H ₂ C=CHCH ₂ O	S	H ₂ C=CHCH ₂ S	S
HC≡CCH ₂ O	O	HC≡CCH ₂ S	O	HC≡CCH ₂ O	S	HC≡CCH ₂ S	S
CF ₃ O	O	CF ₃ S	O	CF ₃ O	S	CF ₃ S	S
(<i>c</i> -propyl)O	O	Cl	O	(<i>c</i> -propyl)O	S	Cl	S

 $R^2 = Me$

X	A	X	A	X	A	X	A
MeO	NH	MeS	NH	MeO	NMe	MeS	NMe

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EtO	NH	EtS	NH	EtO	NMe	EtS	NMe
<i>n</i> -PrO	NH	<i>n</i> -PrS	NH	<i>n</i> -PrO	NMe	<i>n</i> -PrS	NMe
H ₂ C=CHCH ₂ O	NH	H ₂ C=CHCH ₂ S	NH	H ₂ C=CHCH ₂ O	NMe	H ₂ C=CHCH ₂ S	NMe
HC≡CCH ₂ O	NH	HC≡CCH ₂ S	NH	HC≡CCH ₂ O	NMe	HC≡CCH ₂ S	NMe
CF ₃ O	NH	CF ₃ S	NH	CF ₃ O	NMe	CF ₃ S	NMe
(<i>c</i> -propyl)O	NH	Cl	NH	(<i>c</i> -propyl)O	NMe	Cl	NMe

 $R^2 = H$

X	A	X	A	X	A	X	A
MeO	NH	MeS	NH	MeO	NMe	MeS	NMe
EtO	NH	EtS	NH	EtO	NMe	EtS	NMe
<i>n</i> -PrO	NH	<i>n</i> -PrS	NH	<i>n</i> -PrO	NMe	<i>n</i> -PrS	NMe
H ₂ C=CHCH ₂ O	NH	H ₂ C=CHCH ₂ S	NH	H ₂ C=CHCH ₂ O	NMe	H ₂ C=CHCH ₂ S	NMe
HC≡CCH ₂ O	NH	HC≡CCH ₂ S	NH	HC≡CCH ₂ O	NMe	HC≡CCH ₂ S	NMe
CF ₃ O	NH	CF ₃ S	NH	CF ₃ O	NMe	CF ₃ S	NMe
(<i>c</i> -propyl)O	NH	Cl	NH	(<i>c</i> -propyl)O	NMe	Cl	NMe

Table 8

Compounds of Formula I wherein: $E = E^1$, $G = N$, $W = O$, $R^3 = R^4 = H$, $Y = CH_2ON=C(CH_3)$,
 $Z = 4-Me_3Ge-Ph$, the floating double bond is attached to A, and

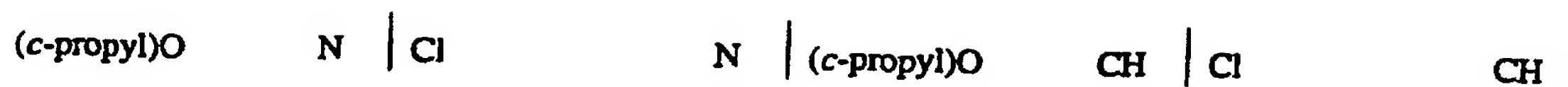
 $R^2 = Me$

X	A	X	A	X	A	X	A
MeO	N	MeS	N	MeO	CH	MeS	CH
EtO	N	EtS	N	EtO	CH	EtS	CH
<i>n</i> -PrO	N	<i>n</i> -PrS	N	<i>n</i> -PrO	CH	<i>n</i> -PrS	CH
H ₂ C=CHCH ₂ O	N	H ₂ C=CHCH ₂ S	N	H ₂ C=CHCH ₂ O	CH	H ₂ C=CHCH ₂ S	CH
HC≡CCH ₂ O	N	HC≡CCH ₂ S	N	HC≡CCH ₂ O	CH	HC≡CCH ₂ S	CH
CF ₃ O	N	CF ₃ S	N	CF ₃ O	CH	CF ₃ S	CH
(<i>c</i> -propyl)O	N	Cl	N	(<i>c</i> -propyl)O	CH	Cl	CH

 $R^2 = Et$

X	A	X	A	X	A	X	A
MeO	N	MeS	N	MeO	CH	MeS	CH
EtO	N	EtS	N	EtO	CH	EtS	CH
<i>n</i> -PrO	N	<i>n</i> -PrS	N	<i>n</i> -PrO	CH	<i>n</i> -PrS	CH
H ₂ C=CHCH ₂ O	N	H ₂ C=CHCH ₂ S	N	H ₂ C=CHCH ₂ O	CH	H ₂ C=CHCH ₂ S	CH
HC≡CCH ₂ O	N	HC≡CCH ₂ S	N	HC≡CCH ₂ O	CH	HC≡CCH ₂ S	CH
CF ₃ O	N	CF ₃ S	N	CF ₃ O	CH	CF ₃ S	CH

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 $R^2 = n\text{-Pr}$

X	A	X	A	X	A	X	A
MeO	N	MeS	N	MeO	CH	MeS	CH
EtO	N	EtS	N	EtO	CH	EtS	CH
<i>n</i> -PrO	N	<i>n</i> -PrS	N	<i>n</i> -PrO	CH	<i>n</i> -PrS	CH
H ₂ C=CHCH ₂ O	N	H ₂ C=CHCH ₂ S	N	H ₂ C=CHCH ₂ O	CH	H ₂ C=CHCH ₂ S	CH
HC≡CCH ₂ O	N	HC≡CCH ₂ S	N	HC≡CCH ₂ O	CH	HC≡CCH ₂ S	CH
CF ₃ O	N	CF ₃ S	N	CF ₃ O	CH	CF ₃ S	CH
(<i>c</i> -propyl)O	N	Cl	N	(<i>c</i> -propyl)O	CH	Cl	CH

 $R^2 = H$

X	A	X	A	X	A	X	A
MeO	N	MeS	N	MeO	CH	MeS	CH
EtO	N	EtS	N	EtO	CH	EtS	CH
<i>n</i> -PrO	N	<i>n</i> -PrS	N	<i>n</i> -PrO	CH	<i>n</i> -PrS	CH
H ₂ C=CHCH ₂ O	N	H ₂ C=CHCH ₂ S	N	H ₂ C=CHCH ₂ O	CH	H ₂ C=CHCH ₂ S	CH
HC≡CCH ₂ O	N	HC≡CCH ₂ S	N	HC≡CCH ₂ O	CH	HC≡CCH ₂ S	CH
CF ₃ O	N	CF ₃ S	N	CF ₃ O	CH	CF ₃ S	CH
(<i>c</i> -propyl)O	N	Cl	N	(<i>c</i> -propyl)O	CH	Cl	CH

 $R^2 = Me$

X	A	X	A	X	A	X	A
MeO	CMe	MeS	CMe	MeO	CEt	MeS	CEt
EtO	CMe	EtS	CMe	EtO	CEt	EtS	CEt
<i>n</i> -PrO	CMe	<i>n</i> -PrS	CMe	<i>n</i> -PrO	CEt	<i>n</i> -PrS	CEt
H ₂ C=CHCH ₂ O	CMe	H ₂ C=CHCH ₂ S	CMe	H ₂ C=CHCH ₂ O	CEt	H ₂ C=CHCH ₂ S	CEt
HC≡CCH ₂ O	CMe	HC≡CCH ₂ S	CMe	HC≡CCH ₂ O	CEt	HC≡CCH ₂ S	CEt
CF ₃ O	CMe	CF ₃ S	CMe	CF ₃ O	CEt	CF ₃ S	CEt
(<i>c</i> -propyl)O	CMe	Cl	CMe	(<i>c</i> -propyl)O	CEt	Cl	CEt

 $R^2 = H$

X	A	X	A	X	A	X	A
MeO	CEt	MeS	CEt	MeO	CMe	MeS	CMe
EtO	CEt	EtS	CEt	EtO	CMe	EtS	CMe
<i>n</i> -PrO	CEt	<i>n</i> -PrS	CEt	<i>n</i> -PrO	CMe	<i>n</i> -PrS	CMe
H ₂ C=CHCH ₂ O	CEt	H ₂ C=CHCH ₂ S	CEt	H ₂ C=CHCH ₂ O	CMe	H ₂ C=CHCH ₂ S	CMe

HC≡CCH ₂ O	CEt	HC≡CCH ₂ S	CEt	HC≡CCH ₂ O	CMe	HC≡CCH ₂ S	CMe
CF ₃ O	CEt	CF ₃ S	CEt	CF ₃ O	CMe	CF ₃ S	CMe
(<i>c</i> -propyl)O	CEt	Cl	CEt	(<i>c</i> -propyl)O	CMe	Cl	CMe

Table 9

Compounds of Formula I wherein: E = E¹, G = C, W = S, R³ = R⁴ = H, Y = CH₂ON=C(CH₃), Z = 3-Me₃Si-Ph, the floating double bond is attached to G, and

R² = Me

X	A	X	A	X	A	X	A
MeO	O	MeS	O	MeO	S	MeS	S
EtO	O	EtS	O	EtO	S	EtS	S
<i>n</i> -PrO	O	<i>n</i> -PrS	O	<i>n</i> -PrO	S	<i>n</i> -PrS	S
H ₂ C=CHCH ₂ O	O	H ₂ C=CHCH ₂ S	O	H ₂ C=CHCH ₂ O	S	H ₂ C=CHCH ₂ S	S
HC≡CCH ₂ O	O	HC≡CCH ₂ S	O	HC≡CCH ₂ O	S	HC≡CCH ₂ S	S
CF ₃ O	O	CF ₃ S	O	CF ₃ O	S	CF ₃ S	S
Cl	O	MeO	NMe	Cl	S	MeS	N- <i>n</i> -Pr

Table 10

Compounds of Formula I wherein: E = E¹, A = N, G = N, W = S, R³ = R⁴ = H, Y = CH₂ON=C(Me), Z = 3-Me₃Si-Ph, the floating double bond is attached to A, and

R² = Me

X	X	X	X
MeO	EtO	<i>n</i> -PrO	H ₂ C=CHCH ₂ O
HC≡CCH ₂ O	CF ₃ O	HCF ₂ O	CF ₃ CH ₂ CH ₂ O
(<i>c</i> -propyl)O	MeS	EtS	<i>n</i> -PrS
H ₂ C=CHCH ₂ S	HC≡CCH ₂ S	CF ₃ S	Cl

Table 11

Compounds of Formula I wherein: E = E¹, G = C, W = S, R³ = R⁴ = H, Y = CH₂ON=C(CH₃), Z = 4-Me₃Si-Ph, the floating double bond is attached to G, and

R² = Me

X	A	X	A	X	A	X	A
MeO	O	MeS	O	MeO	S	MeS	S
EtO	O	EtS	O	EtO	S	EtS	S
<i>n</i> -PrO	O	<i>n</i> -PrS	O	<i>n</i> -PrO	S	<i>n</i> -PrS	S
H ₂ C=CHCH ₂ O	O	H ₂ C=CHCH ₂ S	O	H ₂ C=CHCH ₂ O	S	H ₂ C=CHCH ₂ S	S
HC≡CCH ₂ O	O	HC≡CCH ₂ S	O	HC≡CCH ₂ O	S	HC≡CCH ₂ S	S
CF ₃ O	O	CF ₃ S	O	CF ₃ O	S	CF ₃ S	S

Cl	O	MeO	NMe	MeO	NEt	MeS	N-n-Pr
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Table 12

Compounds of Formula I wherein: $E = E^1$, $A = N$, $G = N$, $W = S$, $R^3 = R^4 = H$, $Y = CH_2ON=C(Me)$, $Z = 3-Me_3Si-Ph$, the floating double bond is attached to A, and $R^2 = Me$

X	X	X	X
MeO	EtO	n-PrO	H ₂ C=CHCH ₂ O
HC≡CCH ₂ O	CF ₃ O	HCF ₂ O	CF ₃ CH ₂ CH ₂ O
(c-propyl)O	MeS	EtS	n-PrS
H ₂ C=CHCH ₂ S	HC≡CCH ₂ S	CF ₃ S	Cl

Table 13

Compounds of Formula I wherein: $E = E^1$, $G = C$, $W = S$, $R^3 = R^4 = H$, $Y = CH_2ON=C(CH_3)$, $Z = 3-Me_3Ge-Ph$, the floating double bond is attached to G, and $R^2 = Me$

X	A	X	A	X	A	X	A
MeO	O	MeS	O	MeO	S	MeS	S
EtO	O	EtS	O	EtO	S	EtS	S
n-PrO	O	n-PrS	O	n-PrO	S	n-PrS	S
H ₂ C=CHCH ₂ O	O	H ₂ C=CHCH ₂ S	O	H ₂ C=CHCH ₂ O	S	H ₂ C=CHCH ₂ S	S
HC≡CCH ₂ O	O	HC≡CCH ₂ S	O	HC≡CCH ₂ O	S	HC≡CCH ₂ S	S
CF ₃ O	O	CF ₃ S	O	CF ₃ O	S	CF ₃ S	S
Cl	O	MeO	NMe	Cl	NEt	MeS	N-n-Pr

Table 14

Compounds of Formula I wherein: $E = E^1$, $A = N$, $G = N$, $W = S$, $R^3 = R^4 = H$, $Y = CH_2ON=C(Me)$, $Z = 3-Me_3Ge-Ph$, the floating double bond is attached to A, and $R^2 = Me$

X	X	X	X
MeO	EtO	n-PrO	H ₂ C=CHCH ₂ O
HC≡CCH ₂ O	CF ₃ O	HCF ₂ O	CF ₃ CH ₂ CH ₂ O
(c-propyl)O	MeS	EtS	n-PrS
H ₂ C=CHCH ₂ S	HC≡CCH ₂ S	CF ₃ S	Cl

Table 15

Compounds of Formula I wherein: $E = E^1$, $G = C$, $W = S$, $R^3 = R^4 = H$, $Y = CH_2ON=C(CH_3)$, $Z = 4-Me_3Ge-Ph$, the floating double bond is attached to G , and $R^2 = Me$

X	A	X	A	X	A	X	A
MeO	O	MeS	O	MeO	S	MeS	S
EtO	O	EtS	O	EtO	S	EtS	S
<i>n</i> -PrO	O	<i>n</i> -PrS	O	<i>n</i> -PrO	S	<i>n</i> -PrS	S
$H_2C=CHCH_2O$	O	$H_2C=CHCH_2S$	O	$H_2C=CHCH_2O$	S	$H_2C=CHCH_2S$	S
$HC\equiv CCH_2O$	O	$HC\equiv CCH_2S$	O	$HC\equiv CCH_2O$	S	$HC\equiv CCH_2S$	S
CF_3O	O	CF_3S	O	CF_3O	S	CF_3S	S
Cl	O	MeO	NMe	Cl	NEt	MeS	N- <i>n</i> -Pr

Table 16

Compounds of Formula I wherein: $E = E^1$, $A = N$, $G = N$, $W = S$, $R^3 = R^4 = H$, $Y = CH_2ON=C(Me)$, $Z = 4-Me_3Ge-Ph$, the floating double bond is attached to A , and $R^2 = Me$

X	X	X	X
MeO	EtO	<i>n</i> -PrO	$H_2C=CHCH_2O$
$HC\equiv CCH_2O$	CF_3O	HCF_2O	$CF_3CH_2CH_2O$
(<i>c</i> -propyl)O	MeS	EtS	<i>n</i> -PrS
$H_2C=CHCH_2S$	$HC\equiv CCH_2S$	CF_3S	Cl

Table 17

Compounds of Formula I wherein: $E = E^1$, $G = C$, $A = W = O$, $X = MeO$, $R^2 = Me$, $Y = CH_2ON=C(Me)$, $Z = 3-Me_3Si-Ph$, the floating double bond is attached to G , and

R^3	R^4	R^3	R^4	R^3	R^4
3-F	H	5- NO_2	H	3-F	5-F
5-F	H	6-Me	H	3-Cl	5-Cl
3-Cl	H	3-Me	H	4-Me	5-Cl
4-Cl	H	4-MeO	H	3-F	5- CF_3
5-Br	H	5- CF_3O	H	3-Cl	5- NO_2
4- CF_3	H	5-allyl	H	6- CF_3O	H
5-CN	H	4-propargyl	H	5- <i>n</i> -Pr	H

Table 18

Compounds of Formula I wherein: $E = E^1$, $A = N$, $G = N$, $W = O$, $X = \text{MeO}$, $R^2 = \text{Me}$,
 $Y = \text{CH}_2\text{ON}=\text{C}(\text{Me})$, $Z = 3\text{-Me}_3\text{Si-Ph}$, the floating double bond is attached to A, and

R^3	R^4	R^3	R^4	R^3	R^4
3-F	H	5-NO ₂	H	3-F	5-F
5-F	H	6-Me	H	3-Cl	5-Cl
3-Cl	H	3-Me	H	4-Me	5-Cl
4-Cl	H	4-MeO	H	3-F	5-CF ₃
5-Br	H	5-CF ₃ O	H	3-Cl	5-NO ₂
4-CF ₃	H	5-allyl	H	6-CF ₃ O	H
5-CN	H	4-propargyl	H	5-n-Pr	H

Table 19

Compounds of Formula I wherein: $E = E^1$, $G = C$, $A = W = O$, $X = \text{MeO}$, $R^2 = \text{Me}$,
 $Y = \text{CH}_2\text{ON}=\text{C}(\text{Me})$, $Z = 4\text{-Me}_3\text{Si-Ph}$, the floating double bond is attached to G, and

R^3	R^4	R^3	R^4	R^3	R^4
3-F	H	5-NO ₂	H	3-F	5-F
5-F	H	6-Me	H	3-Cl	5-Cl
3-Cl	H	3-Me	H	4-Me	5-Cl
4-Cl	H	4-MeO	H	3-F	5-CF ₃
5-Br	H	5-CF ₃ O	H	3-Cl	5-NO ₂
4-CF ₃	H	5-allyl	H	6-CF ₃ O	H
5-CN	H	4-propargyl	H	5-n-Pr	H

Table 20

Compounds of Formula I wherein: $E = E^1$, $A = N$, $G = N$, $W = O$, $X = \text{MeO}$, $R^2 = \text{Me}$,
 $Y = \text{CH}_2\text{ON}=\text{C}(\text{Me})$, $Z = 4\text{-Me}_3\text{Si-Ph}$, the floating double bond is attached to A, and

R^3	R^4	R^3	R^4	R^3	R^4
3-F	H	5-NO ₂	H	3-F	5-F
5-F	H	6-Me	H	3-Cl	5-Cl
3-Cl	H	3-Me	H	4-Me	5-Cl
4-Cl	H	4-MeO	H	3-F	5-CF ₃
5-Br	H	5-CF ₃ O	H	3-Cl	5-NO ₂
4-CF ₃	H	5-allyl	H	6-CF ₃ O	H
5-CN	H	4-propargyl	H	5-n-Pr	H

Table 21

Compounds of Formula I wherein: $E = E^1$, $G = C$, $A = W = O$, $X = \text{MeO}$, $R^2 = \text{Me}$,
 $Y = \text{CH}_2\text{ON}=\text{C}(\text{Me})$, $Z = 3\text{-Me}_3\text{Ge-Ph}$, the floating double bond is attached to G, and

R^3	R^4	R^3	R^4	R^3	R^4
3-F	H	5-NO ₂	H	3-F	5-F
5-F	H	6-Me	H	3-Cl	5-Cl
3-Cl	H	3-Me	H	4-Me	5-Cl
4-Cl	H	4-MeO	H	3-F	5-CF ₃
5-Br	H	5-CF ₃ O	H	3-Cl	5-NO ₂
4-CF ₃	H	5-allyl	H	6-CF ₃ O	H
5-CN	H	4-propargyl	H	5-n-Pr	H

Table 22

Compounds of Formula I wherein: $E = E^1$, $A = N$, $G = N$, $W = O$, $X = \text{MeO}$, $R^2 = \text{Me}$,
 $Y = \text{CH}_2\text{ON}=\text{C}(\text{Me})$, $Z = 3\text{-Me}_3\text{Ge-Ph}$, the floating double bond is attached to A, and

R^3	R^4	R^3	R^4	R^3	R^4
3-F	H	5-NO ₂	H	3-F	5-F
5-F	H	6-Me	H	3-Cl	5-Cl
3-Cl	H	3-Me	H	4-Me	5-Cl
4-Cl	H	4-MeO	H	3-F	5-CF ₃
5-Br	H	5-CF ₃ O	H	3-Cl	5-NO ₂
4-CF ₃	H	5-allyl	H	6-CF ₃ O	H
5-CN	H	4-propargyl	H	5-n-Pr	H

Table 23

Compounds of Formula I wherein: $E = E^1$, $G = C$, $A = W = O$, $X = \text{MeO}$, $R^2 = \text{Me}$,
 $Y = \text{CH}_2\text{ON}=\text{C}(\text{Me})$, $Z = 4\text{-Me}_3\text{Ge-Ph}$, the floating double bond is attached to G, and

R^3	R^4	R^3	R^4	R^3	R^4
3-F	H	5-NO ₂	H	3-F	5-F
5-F	H	6-Me	H	3-Cl	5-Cl
3-Cl	H	3-Me	H	4-Me	5-Cl
4-Cl	H	4-MeO	H	3-F	5-CF ₃
5-Br	H	5-CF ₃ O	H	3-Cl	5-NO ₂
4-CF ₃	H	5-allyl	H	6-CF ₃ O	H
5-CN	H	4-propargyl	H	5-n-Pr	H

Table 24

Compounds of Formula I wherein: $E = E^1$, $A = N$, $G = N$, $W = O$, $X = MeO$, $R^2 = Me$,
 $Y = CH_2ON=C(Me)$, $Z = 4-Me_3Ge-Ph$, the floating double bond is attached to A, and

R^3	R^4	R^3	R^4	R^3	R^4
3-F	H	5-NO ₂	H	3-F	5-F
5-F	H	6-Me	H	3-Cl	5-Cl
3-Cl	H	3-Me	H	4-Me	5-Cl
4-Cl	H	4-MeO	H	3-F	5-CF ₃
5-Br	H	5-CF ₃ O	H	3-Cl	5-NO ₂
4-CF ₃	H	5-allyl	H	6-CF ₃ O	H
5-CN	H	4-propargyl	H	5-n Pr	H

Table 25

Compounds of Formula I wherein: $E = E^1$, $G = C$, $W = O$, $X = MeO$, $R^2 = Me$, $R^3 = R^4 = H$,
 $Z = 3-Me_3Si-Ph$, the floating double bond is attached to G, and

A = O

Y	Y	Y	Y	Y
S	CH ₂ CH ₂	CH(Me)O	SCH ₂	C(Me)=N-O
CH=CH	CH(Me)CH ₂	OCH ₂	SCH(Me)	O-N=CH
C(Me)=CH	CH ₂ CH(Me)	OCH(Me)	CH ₂ O-N=CH	O-N=C(Me)
CH=C(Me)	CH(Me)CH(Me)	CH ₂ S	CH ₂ O-N=C(Me)	CH ₂ OC(=O)NH
C(Me)=C(Me)	CH ₂ O	CH(Me)S	CH=N-O	CHMeOC(O)NH
direct bond	C≡C			

A = S

Y	Y	Y	Y	Y
S	CH ₂ CH ₂	CH(Me)O	SCH ₂	C(Me)=N-O
CH=CH	CH(Me)CH ₂	OCH ₂	SCH(Me)	O-N=CH
C(Me)=CH	CH ₂ CH(Me)	OCH(Me)	CH ₂ O-N=CH	O-N=C(Me)
CH=C(Me)	CH(Me)CH(Me)	CH ₂ S	CH ₂ O-N=C(Me)	CH ₂ OC(=O)NH
C(Me)=C(Me)	CH ₂ O	CH(Me)S	CH=N-O	CHMeOC(O)NH
direct bond	C≡C			

A = NMe

Y	Y	Y	Y	Y
S	CH ₂ CH ₂	CH(Me)O	SCH ₂	C(Me)=N-O
CH=CH	CH(Me)CH ₂	OCH ₂	SCH(Me)	O-N=CH
C(Me)=CH	CH ₂ CH(Me)	OCH(Me)	CH ₂ O-N=CH	O-N=C(Me)
CH=C(Me)	CH(Me)CH(Me)	CH ₂ S	CH ₂ O-N=C(Me)	CH ₂ OC(=O)NH

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C(Me)=C(Me)	CH ₂ O	CH(Me)S	CH=N-O	CHMeOC(O)NH
direct bond	C≡C			

Table 26

Compounds of Formula I wherein: E = E¹, G = N, W = O, X = MeO, R² = Me, R³ = R⁴ = H, Z = 3-Me₃Si-Ph, the floating double bond is attached to A, and

A = N

<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>
S	CH ₂ CH ₂	CH(Me)O	SCH ₂	C(Me)=N-O
CH=CH	CH(Me)CH ₂	OCH ₂	SCH(Me)	O-N=CH
C(Me)=CH	CH ₂ CH(Me)	OCH(Me)	CH ₂ O-N=CH	O-N=C(Me)
CH=C(Me)	CH(Me)CH(Me)	CH ₂ S	CH ₂ O-N=C(Me)	CH ₂ OC(=O)NH
C(Me)=C(Me)	CH ₂ O	CH(Me)S	CH=N-O	CHMeOC(O)NH
direct bond	C≡C			

A = S

<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>
S	CH ₂ CH ₂	CH(Me)O	SCH ₂	C(Me)=N-O
CH=CH	CH(Me)CH ₂	OCH ₂	SCH(Me)	O-N=CH
C(Me)=CH	CH ₂ CH(Me)	OCH(Me)	CH ₂ O-N=CH	O-N=C(Me)
CH=C(Me)	CH(Me)CH(Me)	CH ₂ S	CH ₂ O-N=C(Me)	CH ₂ OC(=O)NH
C(Me)=C(Me)	CH ₂ O	CH(Me)S	CH=N-O	CHMeOC(O)NH
direct bond	C≡C			

A = NMe

<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>
S	CH ₂ CH ₂	CH(Me)O	SCH ₂	C(Me)=N-O
CH=CH	CH(Me)CH ₂	OCH ₂	SCH(Me)	O-N=CH
C(Me)=CH	CH ₂ CH(Me)	OCH(Me)	CH ₂ O-N=CH	O-N=C(Me)
CH=C(Me)	CH(Me)CH(Me)	CH ₂ S	CH ₂ O-N=C(Me)	CH ₂ OC(=O)NH
C(Me)=C(Me)	CH ₂ O	CH(Me)S	CH=N-O	CHMeOC(O)NH
direct bond	C≡C			

Table 27

Compounds of Formula I wherein: E = E¹, G = C, W = O, X = MeO, R² = Me, R³ = R⁴ = H, Z = 4-Me₃Si-Ph, the floating double bond is attached to G, and

A = O

<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>
S	CH ₂ CH ₂	CH(Me)O	SCH ₂	C(Me)=N-O
CH=CH	CH(Me)CH ₂	OCH ₂	SCH(Me)	O-N=CH
C(Me)=CH	CH ₂ CH(Me)	OCH(Me)	CH ₂ O-N=CH	O-N=C(Me)

CH=C(Me)	CH(Me)CH(Me)	CH ₂ S	CH ₂ O-N=C(Me)	CH ₂ OC(=O)NH
C(Me)=C(Me)	CH ₂ O	CH(Me)S	CH=N-O	CHMeOC(O)NH
direct bond	C≡C			
<u>A = S</u>				
<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>
S	CH ₂ CH ₂	CH(Me)O	SCH ₂	C(Me)=N-O
CH=CH	CH(Me)CH ₂	OCH ₂	SCH(Me)	O-N=CH
C(Me)=CH	CH ₂ CH(Me)	OCH(Me)	CH ₂ O-N=CH	O-N=C(Me)
CH=C(Me)	CH(Me)CH(Me)	CH ₂ S	CH ₂ O-N=C(Me)	CH ₂ OC(=O)NH
C(Me)=C(Me)	CH ₂ O	CH(Me)S	CH=N-O	CHMeOC(O)NH
direct bond	C≡C			
<u>A = NMe</u>				
<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>
S	CH ₂ CH ₂	CH(Me)O	SCH ₂	C(Me)=N-O
CH=CH	CH(Me)CH ₂	OCH ₂	SCH(Me)	O-N=CH
C(Me)=CH	CH ₂ CH(Me)	OCH(Me)	CH ₂ O-N=CH	O-N=C(Me)
CH=C(Me)	CH(Me)CH(Me)	CH ₂ S	CH ₂ O-N=C(Me)	CH ₂ OC(=O)NH
C(Me)=C(Me)	CH ₂ O	CH(Me)S	CH=N-O	CHMeOC(O)NH
direct bond	C≡C			

Table 28

Compounds of Formula I wherein: E = E¹, G = N, W = O, X = MeO, R² = Me, R³ = R⁴ = H, Z = 4-Me₃Si-Ph, the floating double bond is attached to A, and

<u>A = N</u>				
<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>
S	CH ₂ CH ₂	CH(Me)O	SCH ₂	C(Me)=N-O
CH=CH	CH(Me)CH ₂	OCH ₂	SCH(Me)	O-N=CH
C(Me)=CH	CH ₂ CH(Me)	OCH(Me)	CH ₂ O-N=CH	O-N=C(Me)
CH=C(Me)	CH(Me)CH(Me)	CH ₂ S	CH ₂ O-N=C(Me)	CH ₂ OC(=O)NH
C(Me)=C(Me)	CH ₂ O	CH(Me)S	CH=N-O	CHMeOC(O)NH
direct bond	C≡C			
<u>A = S</u>				
<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>
S	CH ₂ CH ₂	CH(Me)O	SCH ₂	C(Me)=N-O
CH=CH	CH(Me)CH ₂	OCH ₂	SCH(Me)	O-N=CH
C(Me)=CH	CH ₂ CH(Me)	OCH(Me)	CH ₂ O-N=CH	O-N=C(Me)
CH=C(Me)	CH(Me)CH(Me)	CH ₂ S	CH ₂ O-N=C(Me)	CH ₂ OC(=O)NH
C(Me)=C(Me)	CH ₂ O	CH(Me)S	CH=N-O	CHMeOC(O)NH
direct bond	C≡C			

A = NMe

<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>
S	CH ₂ CH ₂	CH(Me)O	SCH ₂	C(Me)=N-O
CH=CH	CH(Me)CH ₂	OCH ₂	SCH(Me)	O-N=CH
C(Me)=CH	CH ₂ CH(Me)	OCH(Me)	CH ₂ O-N=CH	O-N=C(Me)
CH=C(Me)	CH(Me)CH(Me)	CH ₂ S	CH ₂ O-N=C(Me)	CH ₂ OC(=O)NH
C(Me)=C(Me)	CH ₂ O	CH(Me)S	CH=N-O	CHMeOC(O)NH
direct bond	C≡C			

Table 29

Compounds of Formula I wherein: E = E¹, G = C, W = O, X = MeO, R² = Me, R³ = R⁴ = H,
Z = 3-Me₃Ge-Ph, the floating double bond is attached to G, and

A = O

<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>
S	CH ₂ CH ₂	CH(Me)O	SCH ₂	C(Me)=N-O
CH=CH	CH(Me)CH ₂	OCH ₂	SCH(Me)	O-N=CH
C(Me)=CH	CH ₂ CH(Me)	OCH(Me)	CH ₂ O-N=CH	O-N=C(Me)
CH=C(Me)	CH(Me)CH(Me)	CH ₂ S	CH ₂ O-N=C(Me)	CH ₂ OC(=O)NH
C(Me)=C(Me)	CH ₂ O	CH(Me)S	CH=N-O	CHMeOC(O)NH
direct bond	C≡C			

A = S

<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>
S	CH ₂ CH ₂	CH(Me)O	SCH ₂	C(Me)=N-O
CH=CH	CH(Me)CH ₂	OCH ₂	SCH(Me)	O-N=CH
C(Me)=CH	CH ₂ CH(Me)	OCH(Me)	CH ₂ O-N=CH	O-N=C(Me)
CH=C(Me)	CH(Me)CH(Me)	CH ₂ S	CH ₂ O-N=C(Me)	CH ₂ OC(=O)NH
C(Me)=C(Me)	CH ₂ O	CH(Me)S	CH=N-O	CHMeOC(O)NH
direct bond	C≡C			

A = NMe

<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>
S	CH ₂ CH ₂	CH(Me)O	SCH ₂	C(Me)=N-O
CH=CH	CH(Me)CH ₂	OCH ₂	SCH(Me)	O-N=CH
C(Me)=CH	CH ₂ CH(Me)	OCH(Me)	CH ₂ O-N=CH	O-N=C(Me)
CH=C(Me)	CH(Me)CH(Me)	CH ₂ S	CH ₂ O-N=C(Me)	CH ₂ OC(=O)NH
C(Me)=C(Me)	CH ₂ O	CH(Me)S	CH=N-O	CHMeOC(O)NH
direct bond	C≡C			

Table 30

Compounds of Formula I wherein: $E = E^1$, $G = N$, $W = O$, $X = \text{MeO}$, $R^2 = \text{Me}$, $R^3 = R^4 = H$, $Z = 3\text{-Me}_3\text{Ge-Ph}$, the floating double bond is attached to A, andA = N

<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>
S	CH_2CH_2	$\text{CH}(\text{Me})\text{O}$	SCH_2	$\text{C}(\text{Me})=\text{N-O}$
$\text{CH}=\text{CH}$	$\text{CH}(\text{Me})\text{CH}_2$	OCH_2	$\text{SCH}(\text{Me})$	$\text{O-N}=\text{CH}$
$\text{C}(\text{Me})=\text{CH}$	$\text{CH}_2\text{CH}(\text{Me})$	$\text{OCH}(\text{Me})$	$\text{CH}_2\text{O-N}=\text{CH}$	$\text{O-N}=\text{C}(\text{Me})$
$\text{CH}=\text{C}(\text{Me})$	$\text{CH}(\text{Me})\text{CH}(\text{Me})$	CH_2S	$\text{CH}_2\text{O-N}=\text{C}(\text{Me})$	$\text{CH}_2\text{OC}(=\text{O})\text{NH}$
$\text{C}(\text{Me})=\text{C}(\text{Me})$	CH_2O	$\text{CH}(\text{Me})\text{S}$	CH-N-O	$\text{CHMeOC}(\text{O})\text{NH}$
direct bond	$\text{C}\equiv\text{C}$			

A = S

<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>
S	CH_2CH_2	$\text{CH}(\text{Me})\text{O}$	SCH_2	$\text{C}(\text{Me})=\text{N-O}$
$\text{CH}=\text{CH}$	$\text{CH}(\text{Me})\text{CH}_2$	OCH_2	$\text{SCH}(\text{Me})$	$\text{O-N}=\text{CH}$
$\text{C}(\text{Me})=\text{CH}$	$\text{CH}_2\text{CH}(\text{Me})$	$\text{OCH}(\text{Me})$	$\text{CH}_2\text{O-N}=\text{CH}$	$\text{O-N}=\text{C}(\text{Me})$
$\text{CH}=\text{C}(\text{Me})$	$\text{CH}(\text{Me})\text{CH}(\text{Me})$	CH_2S	$\text{CH}_2\text{O-N}=\text{C}(\text{Me})$	$\text{CH}_2\text{OC}(=\text{O})\text{NH}$
$\text{C}(\text{Me})=\text{C}(\text{Me})$	CH_2O	$\text{CH}(\text{Me})\text{S}$	CH-N-O	$\text{CHMeOC}(\text{O})\text{NH}$
direct bond	$\text{C}\equiv\text{C}$			

A = NMe

<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>
S	CH_2CH_2	$\text{CH}(\text{Me})\text{O}$	SCH_2	$\text{C}(\text{Me})=\text{N-O}$
$\text{CH}=\text{CH}$	$\text{CH}(\text{Me})\text{CH}_2$	OCH_2	$\text{SCH}(\text{Me})$	$\text{O-N}=\text{CH}$
$\text{C}(\text{Me})=\text{CH}$	$\text{CH}_2\text{CH}(\text{Me})$	$\text{OCH}(\text{Me})$	$\text{CH}_2\text{O-N}=\text{CH}$	$\text{O-N}=\text{C}(\text{Me})$
$\text{CH}=\text{C}(\text{Me})$	$\text{CH}(\text{Me})\text{CH}(\text{Me})$	CH_2S	$\text{CH}_2\text{O-N}=\text{C}(\text{Me})$	$\text{CH}_2\text{OC}(=\text{O})\text{NH}$
$\text{C}(\text{Me})=\text{C}(\text{Me})$	CH_2O	$\text{CH}(\text{Me})\text{S}$	CH-N-O	$\text{CHMeOC}(\text{O})\text{NH}$
direct bond	$\text{C}\equiv\text{C}$			

Table 31

Compounds of Formula I wherein: $E = E^1$, $G = C$, $W = O$, $X = \text{MeO}$, $R^2 = \text{Me}$, $R^3 = R^4 = H$, $Z = 4\text{-Me}_3\text{Ge-Ph}$, the floating double bond is attached to G, andA = O

<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>
S	CH_2CH_2	$\text{CH}(\text{Me})\text{O}$	SCH_2	$\text{C}(\text{Me})=\text{N-O}$
$\text{CH}=\text{CH}$	$\text{CH}(\text{Me})\text{CH}_2$	OCH_2	$\text{SCH}(\text{Me})$	$\text{O-N}=\text{CH}$
$\text{C}(\text{Me})=\text{CH}$	$\text{CH}_2\text{CH}(\text{Me})$	$\text{OCH}(\text{Me})$	$\text{CH}_2\text{O-N}=\text{CH}$	$\text{O-N}=\text{C}(\text{Me})$
$\text{CH}=\text{C}(\text{Me})$	$\text{CH}(\text{Me})\text{CH}(\text{Me})$	CH_2S	$\text{CH}_2\text{O-N}=\text{C}(\text{Me})$	$\text{CH}_2\text{OC}(=\text{O})\text{NH}$
$\text{C}(\text{Me})=\text{C}(\text{Me})$	CH_2O	$\text{CH}(\text{Me})\text{S}$	CH-N-O	$\text{CHMeOC}(\text{O})\text{NH}$
direct bond	$\text{C}\equiv\text{C}$			

A = S

<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>
S	CH ₂ CH ₂	CH(Me)O	SCH ₂	C(Me)=N-O
CH=CH	CH(Me)CH ₂	OCH ₂	SCH(Me)	O-N=CH
C(Me)=CH	CH ₂ CH(Me)	OCH(Me)	CH ₂ O-N=CH	O-N=C(Me)
CH=C(Me)	CH(Me)CH(Me)	CH ₂ S	CH ₂ O-N=C(Me)	CH ₂ OC(=O)NH
C(Me)=C(Me)	CH ₂ O	CH(Me)S	CH=N-O	CHMeOC(O)NH
direct bond	C≡C			

A = NMe

<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>
S	CH ₂ CH ₂	CH(Me)O	SCH ₂	C(Me)=N-O
CH=CH	CH(Me)CH ₂	OCH ₂	SCH(Me)	O-N=CH
C(Me)=CH	CH ₂ CH(Me)	OCH(Me)	CH ₂ O-N=CH	O-N=C(Me)
CH=C(Me)	CH(Me)CH(Me)	CH ₂ S	CH ₂ O-N=C(Me)	CH ₂ OC(=O)NH
C(Me)=C(Me)	CH ₂ O	CH(Me)S	CH=N-O	CHMeOC(O)NH
direct bond	C≡C			

Table 32

Compounds of Formula I wherein: E = E¹, G = N, W = O, X = MeO, R² = Me, R³ = R⁴ = H, Z = 4-Me₃Ge-Ph, the floating double bond is attached to A, and

A = N

<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>
S	CH ₂ CH ₂	CH(Me)O	SCH ₂	C(Me)=N-O
CH=CH	CH(Me)CH ₂	OCH ₂	SCH(Me)	O-N=CH
C(Me)=CH	CH ₂ CH(Me)	OCH(Me)	CH ₂ O-N=CH	O-N=C(Me)
CH=C(Me)	CH(Me)CH(Me)	CH ₂ S	CH ₂ O-N=C(Me)	CH ₂ OC(=O)NH
C(Me)=C(Me)	CH ₂ O	CH(Me)S	CH=N-O	CHMeOC(O)NH
direct bond	C≡C			

A = S

<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>
S	CH ₂ CH ₂	CH(Me)O	SCH ₂	C(Me)=N-O
CH=CH	CH(Me)CH ₂	OCH ₂	SCH(Me)	O-N=CH
C(Me)=CH	CH ₂ CH(Me)	OCH(Me)	CH ₂ O-N=CH	O-N=C(Me)
CH=C(Me)	CH(Me)CH(Me)	CH ₂ S	CH ₂ O-N=C(Me)	CH ₂ OC(=O)NH
C(Me)=C(Me)	CH ₂ O	CH(Me)S	CH=N-O	CHMeOC(O)NH
direct bond	C≡C			

A = NMe

<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>
S	CH ₂ CH ₂	CH(Me)O	SCH ₂	C(Me)=N-O
CH=CH	CH(Me)CH ₂	OCH ₂	SCH(Me)	O-N=CH
C(Me)=CH	CH ₂ CH(Me)	OCH(Me)	CH ₂ O-N=CH	O-N=C(Me)
CH=C(Me)	CH(Me)CH(Me)	CH ₂ S	CH ₂ O-N=C(Me)	CH ₂ OC(=O)NH
C(Me)=C(Me)	CH ₂ O	CH(Me)S	CH=N-O	CHMeOC(O)NH
direct bond	C≡C			

Table 33

Compounds of Formula I wherein: E = E¹, G = C, W = O, X = OMe, A = O, R² = Me, R³ and R⁴ = H, the floating double bond is attached to G, and

Y = O

<u>Z</u>	<u>Z</u>	<u>Z</u>	<u>Z</u>
3-Me ₃ Si-Ph	3-Me ₃ Si-2-pyridinyl	3-Me ₃ Si-4-pyridinyl	2-Me-5-Me ₃ Si-Ph
4-Me ₃ Si-Ph	3-Me ₃ Ge-2-pyridinyl	5-Me ₃ Si-3-pyridinyl	2-Me-5-Me ₃ Ge-Ph
3-Me ₃ Ge-Ph	4-Me ₃ Ge-3-pyridinyl	5-Me ₃ Ge-2-pyridinyl	3-TBDMS-Ph
3-(Me ₂ PhSi)-Ph	4-Me ₃ Si-3-pyridinyl	5-Me ₃ Si-2-pyridinyl	3- <i>t</i> -Bu-Ph ₂ Si-Ph

Y = CH₂O

<u>Z</u>	<u>Z</u>	<u>Z</u>	<u>Z</u>
3-Me ₃ Si-Ph	3-Me ₃ Si-2-pyridinyl	3-Me ₃ Si-4-pyridinyl	2-Me-5-Me ₃ Si-Ph
4-Me ₃ Si-Ph	3-Me ₃ Ge-2-pyridinyl	5-Me ₃ Si-3-pyridinyl	2-Me-5-Me ₃ Ge-Ph
3-Me ₃ Ge-Ph	4-Me ₃ Ge-3-pyridinyl	5-Me ₃ Ge-2-pyridinyl	3-TBDMS-Ph
4-Me ₃ Ge-Ph	4-Me ₃ Si-3-pyridinyl	5-Me ₃ Si-2-pyridinyl	3- <i>t</i> -Bu-Ph ₂ Si-Ph

Y = CH₂S

<u>Z</u>	<u>Z</u>	<u>Z</u>	<u>Z</u>
3-Me ₃ Si-Ph	3-Me ₃ Si-2-pyridinyl	3-Me ₃ Si-4-pyridinyl	2-Me-5-Me ₃ Si-Ph
4-Me ₃ Si-Ph	3-Me ₃ Ge-2-pyridinyl	5-Me ₃ Si-3-pyridinyl	2-Me-5-Me ₃ Ge-Ph
3-Me ₃ Ge-Ph	4-Me ₃ Ge-3-pyridinyl	5-Me ₃ Ge-2-pyridinyl	3-TBDMS-Ph
4-Me ₃ Ge-Ph	4-Me ₃ Si-3-pyridinyl	5-Me ₃ Si-2-pyridinyl	3- <i>t</i> -Bu-Ph ₂ Si-Ph

Table 34

Compounds of Formula I wherein: E = E¹, G = N, W = O, A = N, X = OMe, R² = Me, R³ = R⁴ = H, the floating double bond is attached to A, and

Y = O

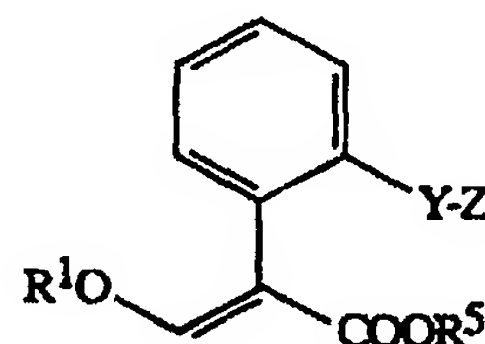
<u>Z</u>	<u>Z</u>	<u>Z</u>	<u>Z</u>
3-Me ₃ Si-Ph	3-Me ₃ Si-2-pyridinyl	3-Me ₃ Si-4-pyridinyl	2-Me-5-Me ₃ Si-Ph
4-Me ₃ Si-Ph	3-Me ₃ Ge-2-pyridinyl	5-Me ₃ Si-3-pyridinyl	2-Me-5-Me ₃ Ge-Ph
3-Me ₃ Ge-Ph	4-Me ₃ Ge-3-pyridinyl	5-Me ₃ Ge-2-pyridinyl	3-TBDMS-Ph
3-(Me ₂ PhSi)-Ph	4-Me ₃ Si-3-pyridinyl	5-Me ₃ Si-2-pyridinyl	3- <i>t</i> -Bu-Ph ₂ Si-Ph

Y = CH₂O

Z	Z	Z	Z
3-Me ₃ Si-Ph	3-Me ₃ Si-2-pyridinyl	3-Me ₃ Si-4-pyridinyl	2-Me-5-Me ₃ Si-Ph
4-Me ₃ Si-Ph	3-Me ₃ Ge-2-pyridinyl	5-Me ₃ Si-3-pyridinyl	2-Me-5-Me ₃ Ge-Ph
3-Me ₃ Ge-Ph	4-Me ₃ Ge-3-pyridinyl	5-Me ₃ Ge-2-pyridinyl	3-TBDMS-Ph
4-Me ₃ Ge-Ph	4-Me ₃ Si-3-pyridinyl	5-Me ₃ Si-2-pyridinyl	3- <i>t</i> -Bu-Ph ₂ Si-Ph

Y = CH₂S

Z	Z	Z	Z
3-Me ₃ Si-Ph	3-Me ₃ Si-2-pyridinyl	3-Me ₃ Si-4-pyridinyl	2-Me-5-Me ₃ Si-Ph
4-Me ₃ Si-Ph	3-Me ₃ Ge-2-pyridinyl	5-Me ₃ Si-3-pyridinyl	2-Me-5-Me ₃ Ge-Ph
3-Me ₃ Ge-Ph	4-Me ₃ Ge-3-pyridinyl	5-Me ₃ Ge-2-pyridinyl	3-TBDMS-Ph
4-Me ₃ Ge-Ph	4-Me ₃ Si-3-pyridinyl	5-Me ₃ Si-2-pyridinyl	3- <i>t</i> -Bu-Ph ₂ Si-Ph

Formula I where E is E²Table 35Compounds of Formula I wherein: E = E², R¹ = Me, R⁵ = Me, Y = CH₂ON=C(CH₃), and

Z	Z	Z	Z
3-Me ₃ Si-Ph	3-Me ₃ Si-2-pyridinyl	3-Me ₃ Si-4-pyridinyl	2-Me-5-Me ₃ Si-Ph
4-Me ₃ Si-Ph	3-Me ₃ Ge-2-pyridinyl	5-Me ₃ Si-3-pyridinyl	2-Me-5-Me ₃ Ge-Ph
3-Me ₃ Ge-Ph	4-Me ₃ Ge-3-pyridinyl	5-Me ₃ Ge-2-pyridinyl	3-TBDMS-Ph
4-Me ₃ Ge-Ph	4-Me ₃ Si-3-pyridinyl	5-Me ₃ Si-2-pyridinyl	3- <i>t</i> -Bu-Ph ₂ Si-Ph

Table 36Compounds of Formula I wherein: E = E², R¹ = Me, R⁵ = Me, Y = CH₂O, and

Z	Z	Z	Z
3-Me ₃ Si-Ph	3-Me ₃ Si-2-pyridinyl	3-Me ₃ Si-4-pyridinyl	2-Me-5-Me ₃ Si-Ph
4-Me ₃ Si-Ph	3-Me ₃ Ge-2-pyridinyl	5-Me ₃ Si-3-pyridinyl	2-Me-5-Me ₃ Ge-Ph
3-Me ₃ Ge-Ph	4-Me ₃ Ge-3-pyridinyl	5-Me ₃ Ge-2-pyridinyl	3-TBDMS-Ph
4-Me ₃ Ge-Ph	4-Me ₃ Si-3-pyridinyl	5-Me ₃ Si-2-pyridinyl	3- <i>t</i> -Bu-Ph ₂ Si-Ph

Table 37Compounds of Formula I wherein: E = E², R¹ = Me, R⁵ = Me, Y = CH₂S, and

Z	Z	Z	Z
3-Me ₃ Si-Ph	3-Me ₃ Si-2-pyridinyl	3-Me ₃ Si-4-pyridinyl	2-Me-5-Me ₃ Si-Ph
4-Me ₃ Si-Ph	3-Me ₃ Ge-2-pyridinyl	5-Me ₃ Si-3-pyridinyl	2-Me-5-Me ₃ Ge-Ph

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3-Me ₃ Ge-Ph	4-Me ₃ Ge-3-pyridinyl	5-Me ₃ Ge-2-pyridinyl	3-TBDMS-Ph
4-Me ₃ Ge-Ph	4-Me ₃ Si-3-pyridinyl	5-Me ₃ Si-2-pyridinyl	3- <i>t</i> -Bu-Ph ₂ Si-Ph

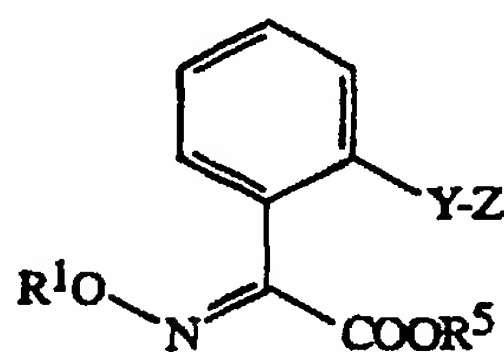
Formula I where E is E³

Table 38

Compounds of Formula I wherein: E = E³, R¹ = Me, R⁵ = Me, Y = CH₂ON=C(CH₃), and

Z	Z	Z	Z
3-Me ₃ Si-Ph	3-Me ₃ Si-2-pyridinyl	3-Me ₃ Si-4-pyridinyl	2-Me-5-Me ₃ Si-Ph
4-Me ₃ Si-Ph	3-Me ₃ Ge-2-pyridinyl	5-Me ₃ Si-3-pyridinyl	2-Me-5-Me ₃ Ge-Ph
3-Me ₃ Ge-Ph	4-Me ₃ Ge-3-pyridinyl	5-Me ₃ Ge-2-pyridinyl	3-(Me ₂ PhSi)-Ph
4-Me ₃ Ge-Ph	4-Me ₃ Si-3-pyridinyl	5-Me ₃ Si-2-pyridinyl	3- <i>t</i> -Bu-Ph ₂ Si-Ph

Table 39

Compounds of Formula I wherein: E = E³, R¹ = Me, R⁵ = Me, Y = CH₂O, and

Z	Z	Z	Z
3-Me ₃ Si-Ph	3-Me ₃ Si-2-pyridinyl	3-Me ₃ Si-4-pyridinyl	2-Me-5-Me ₃ Si-Ph
4-Me ₃ Si-Ph	3-Me ₃ Ge-2-pyridinyl	5-Me ₃ Si-3-pyridinyl	2-Me-5-Me ₃ Ge-Ph
3-Me ₃ Ge-Ph	4-Me ₃ Ge-3-pyridinyl	5-Me ₃ Ge-2-pyridinyl	3-TBDMS-Ph
4-Me ₃ Ge-Ph	4-Me ₃ Si-3-pyridinyl	5-Me ₃ Si-2-pyridinyl	3- <i>t</i> -Bu-Ph ₂ Si-Ph

Table 40

Compounds of Formula I wherein: E = E³, R¹ = Me, R⁵ = Me, Y = CH₂S, and

Z	Z	Z	Z
3-Me ₃ Si-Ph	3-Me ₃ Si-2-pyridinyl	3-Me ₃ Si-4-pyridinyl	2-Me-5-Me ₃ Si-Ph
4-Me ₃ Si-Ph	3-Me ₃ Ge-2-pyridinyl	5-Me ₃ Si-3-pyridinyl	2-Me-5-Me ₃ Ge-Ph
3-Me ₃ Ge-Ph	4-Me ₃ Ge-3-pyridinyl	5-Me ₃ Ge-2-pyridinyl	3-TBDMS-Ph
4-Me ₃ Ge-Ph	4-Me ₃ Si-3-pyridinyl	5-Me ₃ Si-2-pyridinyl	3- <i>t</i> -Bu-Ph ₂ Si-Ph

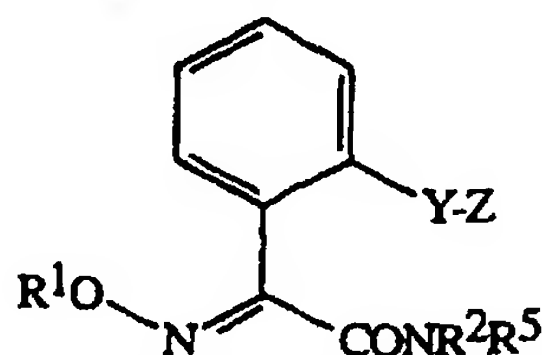
Formula I where E is E⁴

Table 41

Compounds of Formula I wherein: $E = E^4$, $R^1 = \text{Me}$, $R^2 = \text{H}$, $R^5 = \text{Me}$, $Y = \text{CH}_2\text{ON}=\text{C}(\text{CH}_3)$, and

Z	Z	Z	Z
3-Me ₃ Si-Ph	3-Me ₃ Si-2-pyridinyl	3-Me ₃ Si-4-pyridinyl	2-Me-5-Me ₃ Si-Ph
4-Me ₃ Si-Ph	3-Me ₃ Ge-2-pyridinyl	5-Me ₃ Si-3-pyridinyl	2-Me-5-Me ₃ Ge-Ph
3-Me ₃ Ge-Ph	4-Me ₃ Ge-3-pyridinyl	5-Me ₃ Ge-2-pyridinyl	3-TBDMS-Ph
4-Me ₃ Ge-Ph	4-Me ₃ Si-3-pyridinyl	5-Me ₃ Si-2-pyridinyl	3- <i>t</i> -Bu-Ph ₂ Si-Ph

Table 42

Compounds of Formula I wherein: $E = E^4$, $R^1 = \text{Me}$, $R^2 = \text{H}$, $R^5 = \text{Me}$, $Y = \text{CH}_2\text{O}$, and

Z	Z
3-Me ₃ Ge-Ph	4-Me ₃ Ge-3-pyridinyl
4-Me ₃ Ge-Ph	5-Me ₃ Ge-2-pyrimidinyl
3-Me ₃ Ge-2-pyridinyl	2-Me-5-Me ₃ Ge-Ph

Table 43

Compounds of Formula I wherein: $E = E^4$, $R^1 = \text{Me}$, $R^2 = \text{H}$, $R^5 = \text{Me}$, $Y = \text{CH}_2\text{S}$, and

Z	Z
3-Me ₃ Ge-Ph	4-Me ₃ Ge-3-pyridinyl
4-Me ₃ Ge-Ph	5-Me ₃ Ge-2-pyrimidinyl
3-Me ₃ Ge-2-pyridinyl	2-Me-5-Me ₃ Ge-Ph

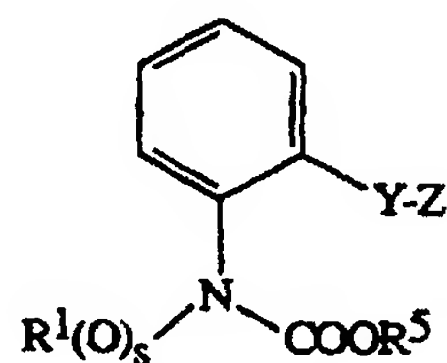
Formula I where E is E^5

Table 44

Compounds of Formula I wherein: $E = E^5$, $R^1 = \text{Me}$, $R^5 = \text{Me}$, $Y = \text{CH}_2\text{ON}=\text{C}(\text{CH}_3)$, $s = 0$, and

Z	Z	Z	Z
3-Me ₃ Si-Ph	3-Me ₃ Si-2-pyridinyl	3-Me ₃ Si-4-pyridinyl	2-Me-5-Me ₃ Si-Ph
4-Me ₃ Si-Ph	3-Me ₃ Ge-2-pyridinyl	5-Me ₃ Si-3-pyridinyl	2-Me-5-Me ₃ Ge-Ph
3-Me ₃ Ge-Ph	4-Me ₃ Ge-3-pyridinyl	5-Me ₃ Ge-2-pyridinyl	3-TBDMS-Ph
4-Me ₃ Ge-Ph	4-Me ₃ Si-3-pyridinyl	5-Me ₃ Si-2-pyridinyl	3- <i>t</i> -Bu-Ph ₂ Si-Ph

Table 45

Compounds of Formula I wherein: $E = E^5$, $R^1 = CH_2C\equiv CH$, $R^5 = Me$, $Y = CH_2ON=C(CH_3)$, $s = 0$, and

Z	Z	Z	Z
3-Me ₃ Si-Ph	3-Me ₃ Si-2-pyridinyl	3-Me ₃ Si-4-pyridinyl	2-Me-5-Me ₃ Si-Ph
4-Me ₃ Si-Ph	3-Me ₃ Ge-2-pyridinyl	5-Me ₃ Si-3-pyridinyl	2-Me-5-Me ₃ Ge-Ph
3-Me ₃ Ge-Ph	4-Me ₃ Ge-3-pyridinyl	5-Me ₃ Ge-2-pyridinyl	3-TBDMS-Ph
4-Me ₃ Ge-Ph	4-Me ₃ Si-3-pyridinyl	5-Me ₃ Si-2-pyridinyl	3- <i>t</i> -Bu-Ph ₂ Si-Ph

Table 46

Compounds of Formula I wherein: $E = E^5$, $R^1 = Me$, $R^5 = Me$, $Y = CH_2O$, $s = 0$, and

Z	Z	Z	Z
3-Me ₃ Si-Ph	3-Me ₃ Si-2-pyridinyl	3-Me ₃ Si-4-pyridinyl	2-Me-5-Me ₃ Si-Ph
4-Me ₃ Si-Ph	3-Me ₃ Ge-2-pyridinyl	5-Me ₃ Si-3-pyridinyl	2-Me-5-Me ₃ Ge-Ph
3-Me ₃ Ge-Ph	4-Me ₃ Ge-3-pyridinyl	5-Me ₃ Ge-2-pyridinyl	3-TBDMS-Ph
4-Me ₃ Ge-Ph	4-Me ₃ Si-3-pyridinyl	5-Me ₃ Si-2-pyridinyl	3- <i>t</i> -Bu-Ph ₂ Si-Ph

Table 47

Compounds of Formula I wherein: $E = E^5$, $R^1 = CH_2C\equiv CH$, $R^5 = Me$, $Y = CH_2O$, $s = 0$, and

Z	Z	Z	Z
3-Me ₃ Si-Ph	3-Me ₃ Si-2-pyridinyl	3-Me ₃ Si-4-pyridinyl	2-Me-5-Me ₃ Si-Ph
4-Me ₃ Si-Ph	3-Me ₃ Ge-2-pyridinyl	5-Me ₃ Si-3-pyridinyl	2-Me-5-Me ₃ Ge-Ph
3-Me ₃ Ge-Ph	4-Me ₃ Ge-3-pyridinyl	5-Me ₃ Ge-2-pyridinyl	3-TBDMS-Ph
4-Me ₃ Ge-Ph	4-Me ₃ Si-3-pyridinyl	5-Me ₃ Si-2-pyridinyl	3- <i>t</i> -Bu-Ph ₂ Si-Ph

Table 48

Compounds of Formula I wherein: $E = E^5$, $R^1 = Me$, $R^5 = Me$, $Y = CH_2S$, $s = 0$, and

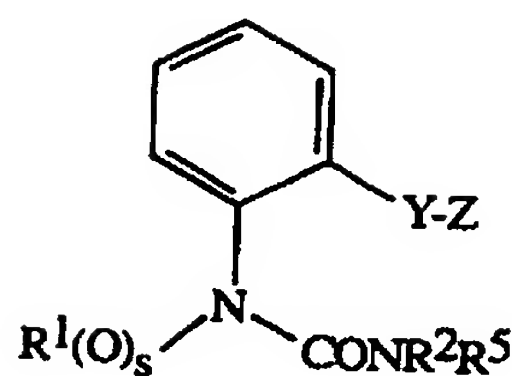
Z	Z	Z	Z
3-Me ₃ Si-Ph	3-Me ₃ Si-2-pyridinyl	3-Me ₃ Si-4-pyridinyl	2-Me-5-Me ₃ Si-Ph
4-Me ₃ Si-Ph	3-Me ₃ Ge-2-pyridinyl	5-Me ₃ Si-3-pyridinyl	2-Me-5-Me ₃ Ge-Ph
3-Me ₃ Ge-Ph	4-Me ₃ Ge-3-pyridinyl	5-Me ₃ Ge-2-pyridinyl	3-TBDMS-Ph
4-Me ₃ Ge-Ph	4-Me ₃ Si-3-pyridinyl	5-Me ₃ Si-2-pyridinyl	3- <i>t</i> -Bu-Ph ₂ Si-Ph

Table 49

Compounds of Formula I wherein: $E = E^5$, $R^1 = CH_2C\equiv CH$, $R^5 = Me$, $Y = CH_2S$, $s = 0$, and

Z	Z	Z	Z
3-Me ₃ Si-Ph	3-Me ₃ Si-2-pyridinyl	3-Me ₃ Si-4-pyridinyl	2-Me-5-Me ₃ Si-Ph
4-Me ₃ Si-Ph	3-Me ₃ Ge-2-pyridinyl	5-Me ₃ Si-3-pyridinyl	2-Me-5-Me ₃ Ge-Ph
3-Me ₃ Ge-Ph	4-Me ₃ Ge-3-pyridinyl	5-Me ₃ Ge-2-pyridinyl	3-TBDMS-Ph
4-Me ₃ Ge-Ph	4-Me ₃ Si-3-pyridinyl	5-Me ₃ Si-2-pyridinyl	3- <i>t</i> -Bu-Ph ₂ Si-Ph

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Formula I where E is E⁶Table 50Compounds of Formula I wherein: E = E⁶, R¹ = CH₂C≡CH, R² = H, R⁵ = Me, Y = CH₂ON=C(CH₃), s = 0, and

Z	Z	Z	Z
3-Me ₃ Si-Ph	3-Me ₃ Si-2-pyridinyl	3-Me ₃ Si-4-pyridinyl	2-Me-5-Me ₃ Si-Ph
4-Me ₃ Si-Ph	3-Me ₃ Ge-2-pyridinyl	5-Me ₃ Si-3-pyridinyl	2-Me-5-Me ₃ Ge-Ph
3-Me ₃ Ge-Ph	4-Me ₃ Ge-3-pyridinyl	5-Me ₃ Ge-2-pyridinyl	3-TBDMS-Ph
4-Me ₃ Ge-Ph	4-Me ₃ Si-3-pyridinyl	5-Me ₃ Si-2-pyridinyl	3- <i>t</i> -Bu-Ph ₂ Si-Ph

Table 51Compounds of Formula I wherein: E = E⁶, R¹ = Me, R² = H, R⁵ = Me, Y = CH₂ON=C(CH₃), s = 0, and

Z	Z	Z	Z
3-Me ₃ Si-Ph	3-Me ₃ Si-2-pyridinyl	3-Me ₃ Si-4-pyridinyl	2-Me-5-Me ₃ Si-Ph
4-Me ₃ Si-Ph	3-Me ₃ Ge-2-pyridinyl	5-Me ₃ Si-3-pyridinyl	2-Me-5-Me ₃ Ge-Ph
3-Me ₃ Ge-Ph	4-Me ₃ Ge-3-pyridinyl	5-Me ₃ Ge-2-pyridinyl	3-TBDMS-Ph
4-Me ₃ Ge-Ph	4-Me ₃ Si-3-pyridinyl	5-Me ₃ Si-2-pyridinyl	3- <i>t</i> -Bu-Ph ₂ Si-Ph

Table 52Compounds of Formula I wherein: E = E⁶, R¹ = CH₂C≡CH, R² = H, R⁵ = Me, Y = CH₂O, s = 0, and

Z	Z	Z	Z
3-Me ₃ Si-Ph	3-Me ₃ Si-2-pyridinyl	3-Me ₃ Si-4-pyridinyl	2-Me-5-Me ₃ Si-Ph
4-Me ₃ Si-Ph	3-Me ₃ Ge-2-pyridinyl	5-Me ₃ Si-3-pyridinyl	2-Me-5-Me ₃ Ge-Ph
3-Me ₃ Ge-Ph	4-Me ₃ Ge-3-pyridinyl	5-Me ₃ Ge-2-pyridinyl	3-TBDMS-Ph
4-Me ₃ Ge-Ph	4-Me ₃ Si-3-pyridinyl	5-Me ₃ Si-2-pyridinyl	3- <i>t</i> -Bu-Ph ₂ Si-Ph

Table 53Compounds of Formula I wherein: E = E⁶, R¹ = Me, R² = H, R⁵ = Me, Y = CH₂O, s = 0, and

Z	Z	Z	Z
3-Me ₃ Si-Ph	3-Me ₃ Si-2-pyridinyl	3-Me ₃ Si-4-pyridinyl	2-Me-5-Me ₃ Si-Ph
4-Me ₃ Si-Ph	3-Me ₃ Ge-2-pyridinyl	5-Me ₃ Si-3-pyridinyl	2-Me-5-Me ₃ Ge-Ph
3-Me ₃ Ge-Ph	4-Me ₃ Ge-3-pyridinyl	5-Me ₃ Ge-2-pyridinyl	3-TBDMS-Ph
4-Me ₃ Ge-Ph	4-Me ₃ Si-3-pyridinyl	5-Me ₃ Si-2-pyridinyl	3- <i>t</i> -Bu-Ph ₂ Si-Ph

Table 54

Compounds of Formula I wherein: $E = E^6$, $R^1 = CH_2C\equiv CH$, $R^2 = H$, $R^5 = Me$, $Y = CH_2S$, $s = 0$, and

Z	Z	Z	Z
3-Me ₃ Si-Ph	3-Me ₃ Si-2-pyridinyl	3-Me ₃ Si-4-pyridinyl	2-Me-5-Me ₃ Si-Ph
4-Me ₃ Si-Ph	3-Me ₃ Ge-2-pyridinyl	5-Me ₃ Si-3-pyridinyl	2-Me-5-Me ₃ Ge-Ph
3-Me ₃ Ge-Ph	4-Me ₃ Ge-3-pyridinyl	5-Me ₃ Ge-2-pyridinyl	3-TBDMS-Ph
4-Me ₃ Ge-Ph	4-Me ₃ Si-3-pyridinyl	5-Me ₃ Si-2-pyridinyl	3- <i>t</i> -Bu-Ph ₂ Si-Ph

Table 55

Compounds of Formula I wherein: $E = E^6$, $R^1 = Me$, $R^2 = H$, $R^5 = Me$, $Y = CH_2S$, $s = 0$, and

Z	Z	Z	Z
3-Me ₃ Si-Ph	3-Me ₃ Si-2-pyridinyl	3-Me ₃ Si-4-pyridinyl	2-Me-5-Me ₃ Si-Ph
4-Me ₃ Si-Ph	3-Me ₃ Ge-2-pyridinyl	5-Me ₃ Si-3-pyridinyl	2-Me-5-Me ₃ Ge-Ph
3-Me ₃ Ge-Ph	4-Me ₃ Ge-3-pyridinyl	5-Me ₃ Ge-2-pyridinyl	3-TBDMS-Ph
4-Me ₃ Ge-Ph	4-Me ₃ Si-3-pyridinyl	5-Me ₃ Si-2-pyridinyl	3- <i>t</i> -Bu-Ph ₂ Si-Ph

Table 56

Compounds of Formula I wherein: $E = E^1$, $A = O$, $G = C$, $W = O$, $X = MeO$, $R^3 = R^4 = H$, $R^2 = Me$, the floating double bond is attached to G, and

Y-Z	Y-Z	Y-Z

Table 57

Compounds of Formula I wherein: $E = E^1$, $A = N$, $G = N$, $W = O$, $X = MeO$, $R^3 = R^4 = H$, $R^2 = Me$, the floating double bond is attached to G, and

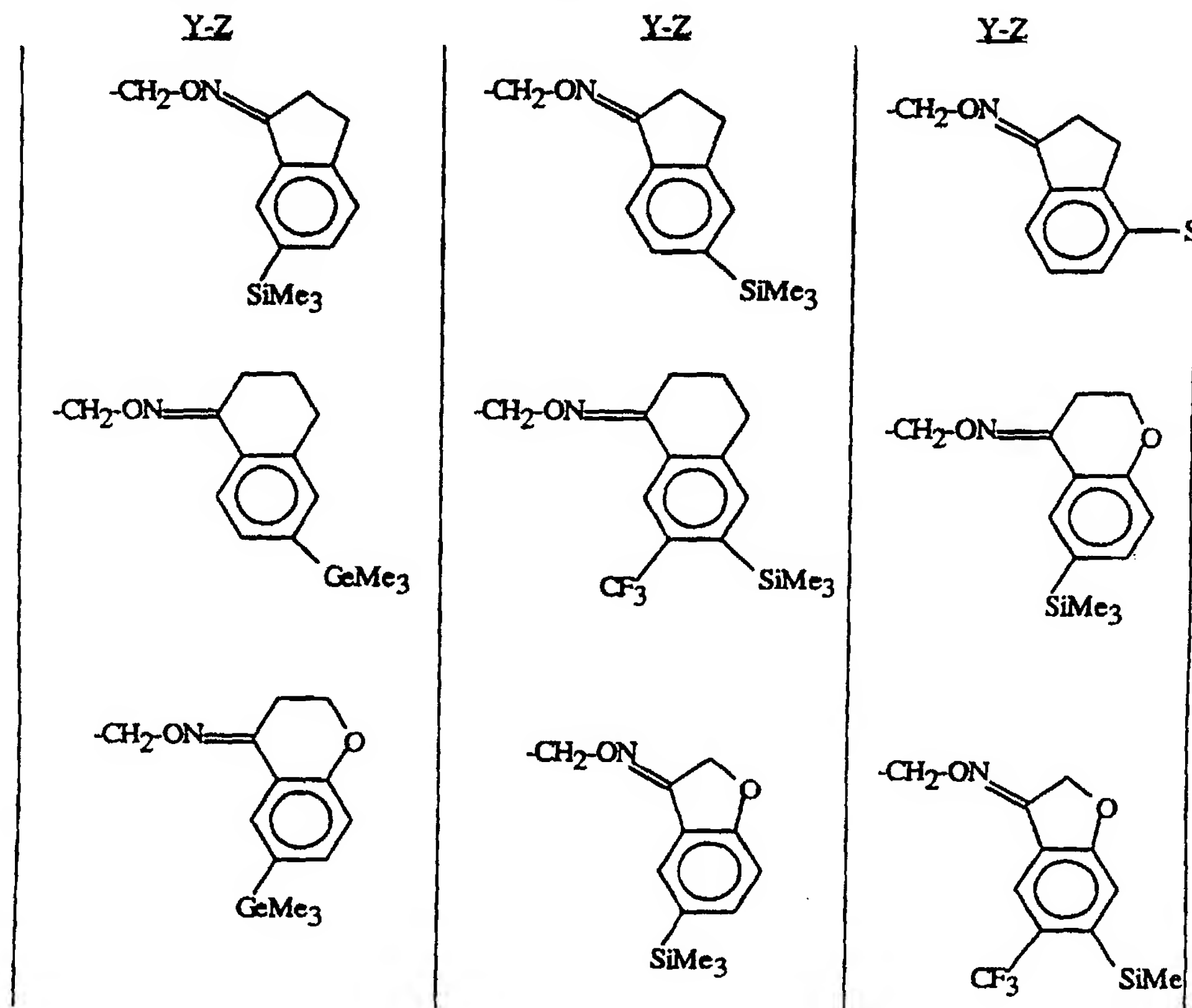
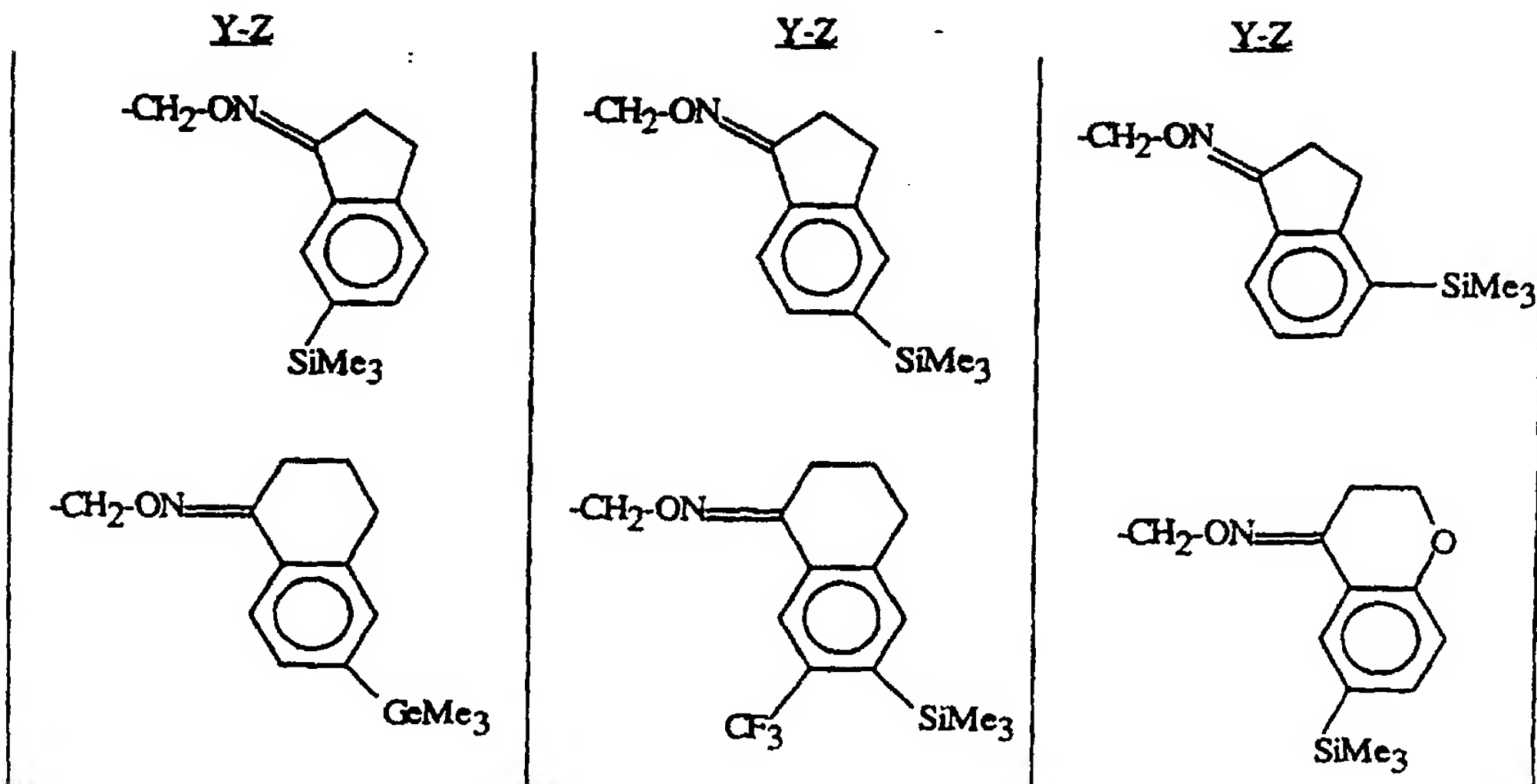


Table 58

Compounds of Formula I wherein: $E = E^2$, $R^1 = Me$, $R^5 = Me$, and



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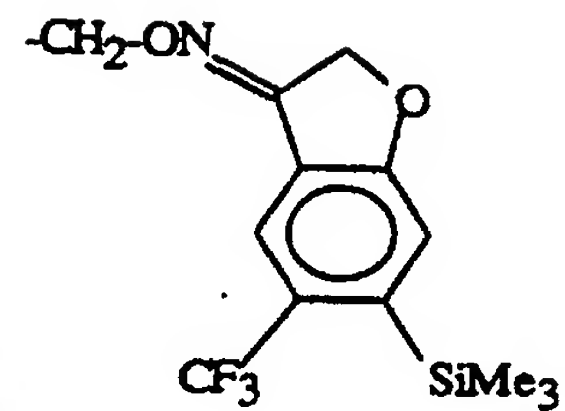
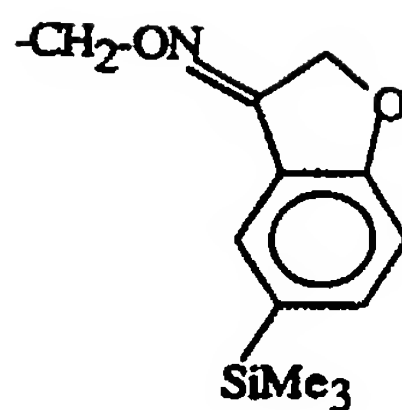
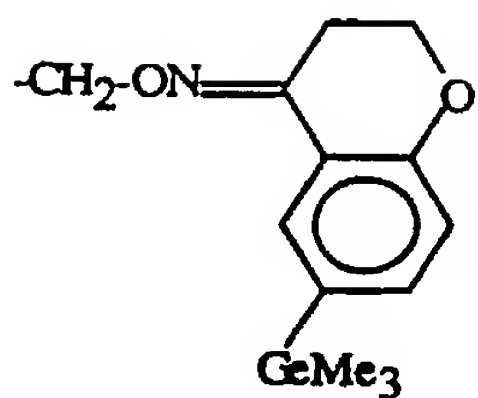


Table 59

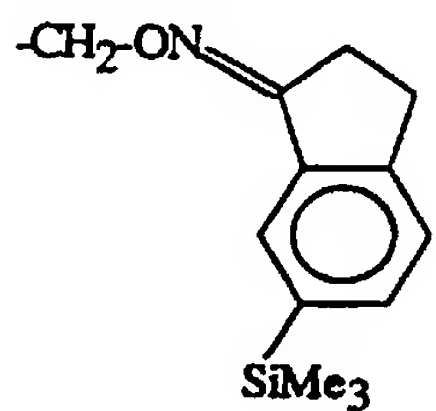
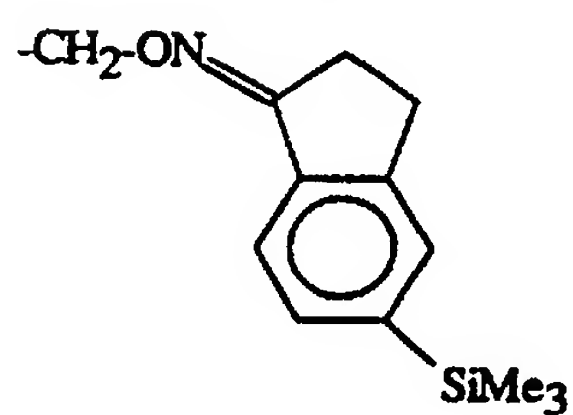
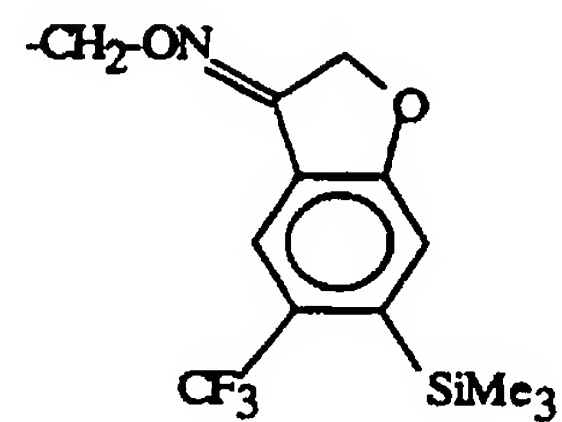
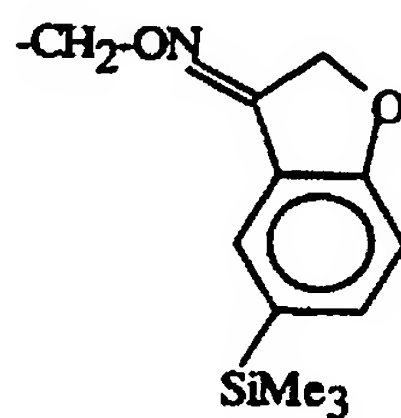
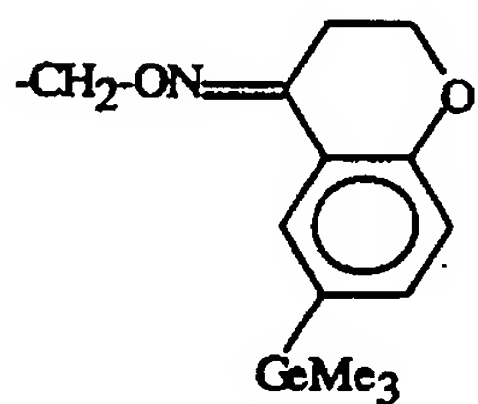
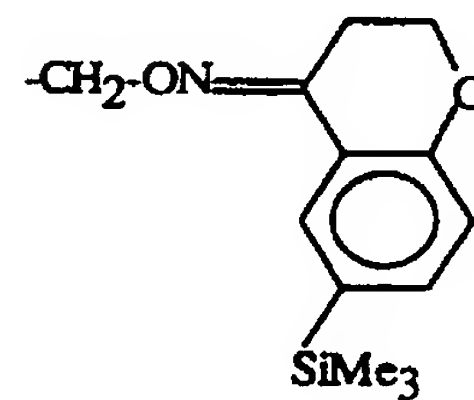
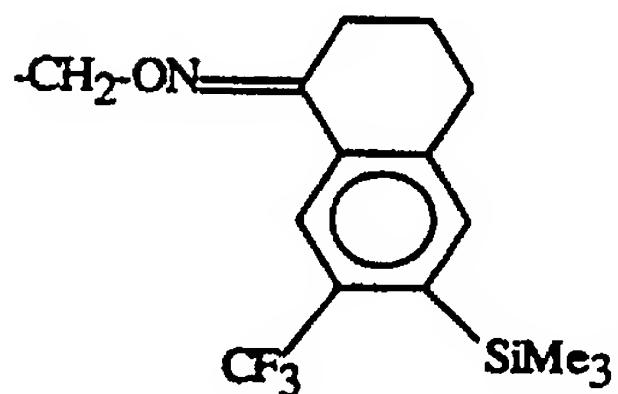
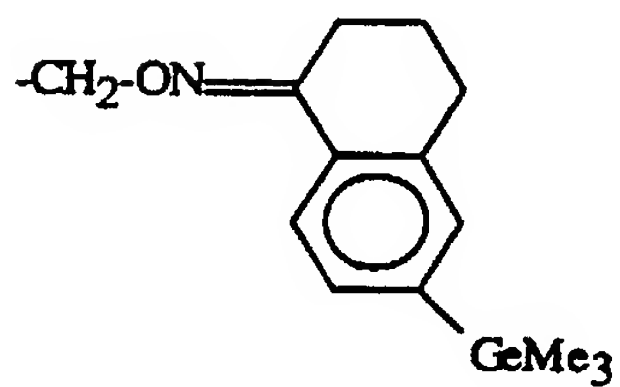
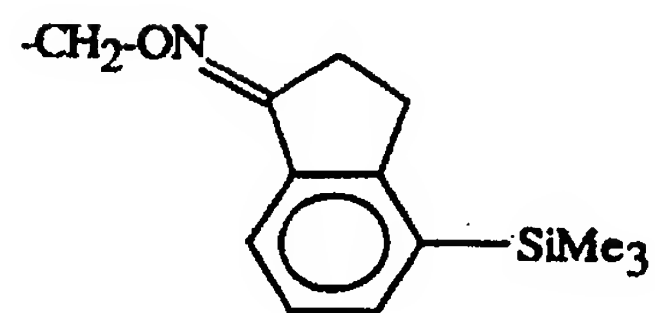
Compounds of Formula I wherein: $\text{E} = \text{E}^3$, $\text{R}^1 = \text{Me}$, $\text{R}^5 = \text{Me}$, andY-ZY-ZY-Z

Table 60

Compounds of Formula I wherein: $E = E^4$, $R^1 = \text{Me}$, $R^2 = \text{H}$, $R^5 = \text{Me}$, and

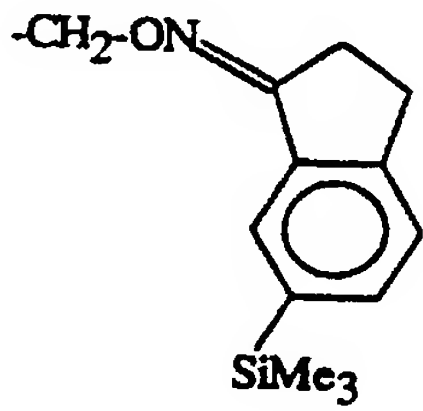
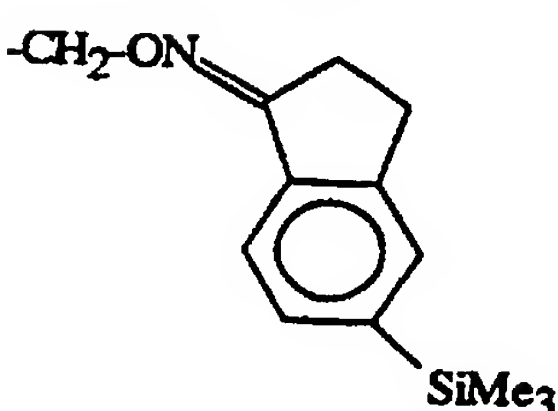
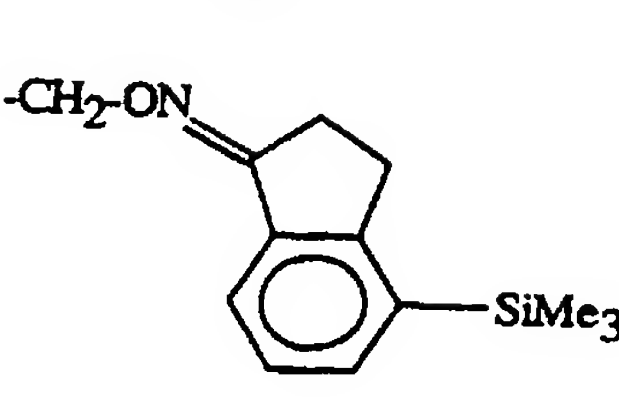
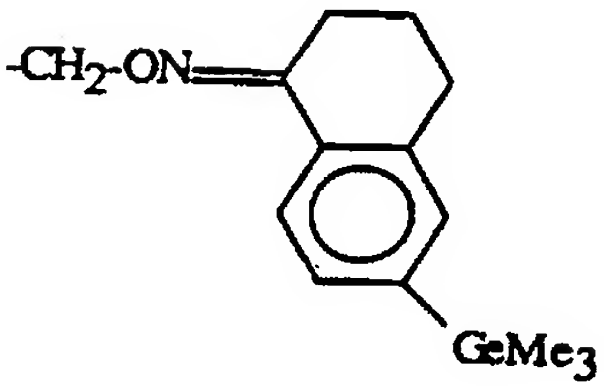
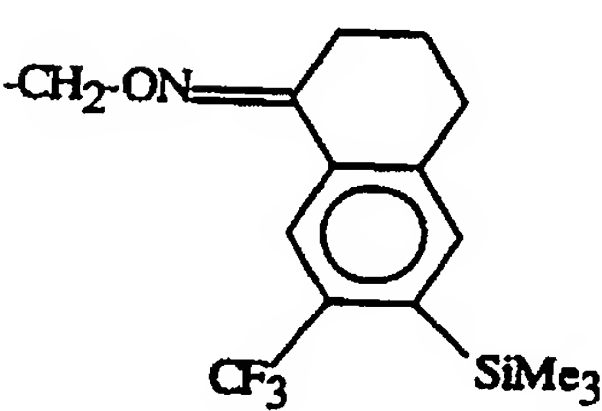
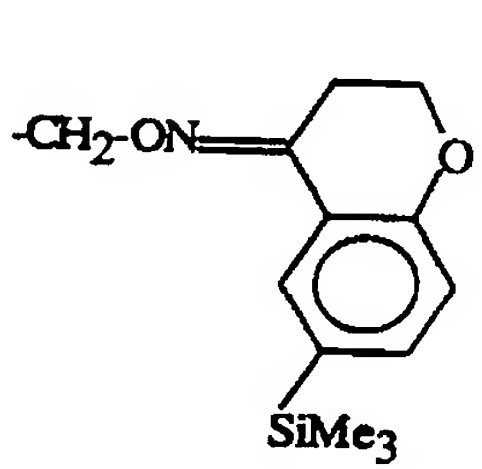
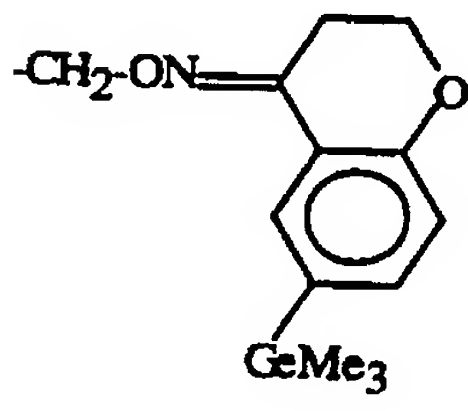
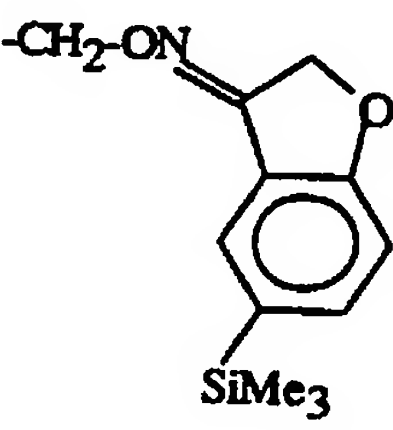
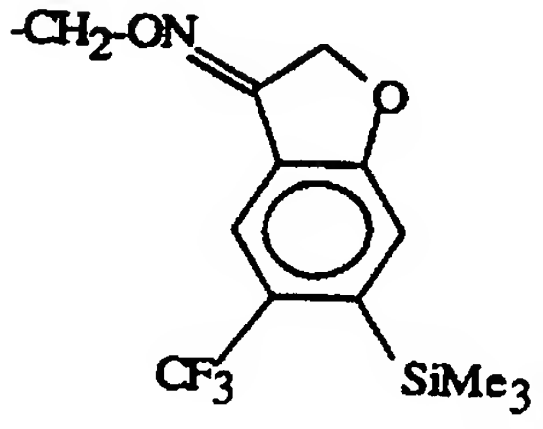
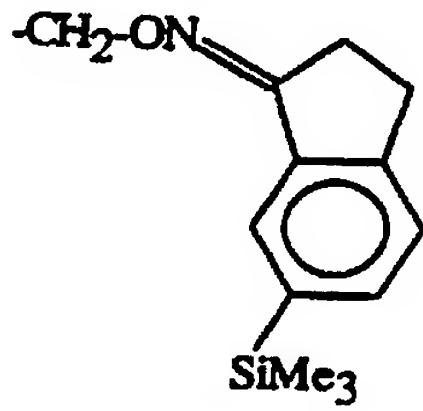
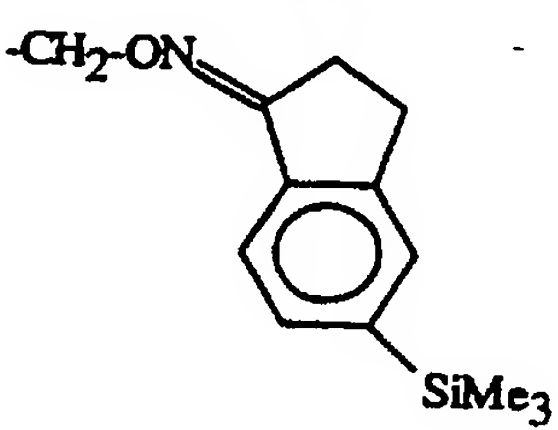
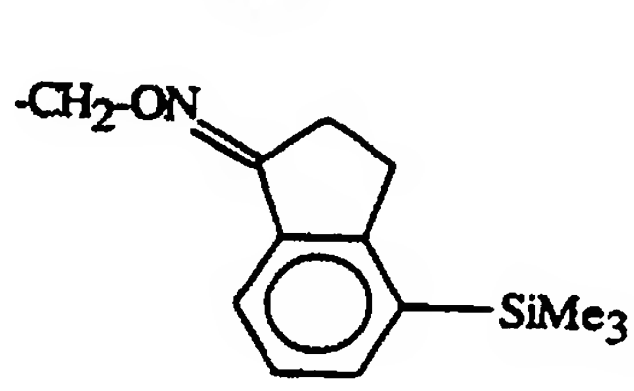
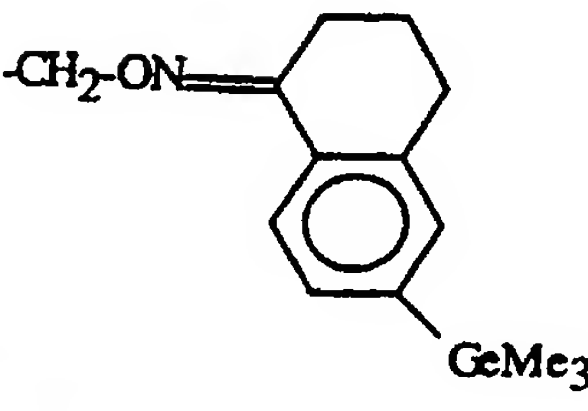
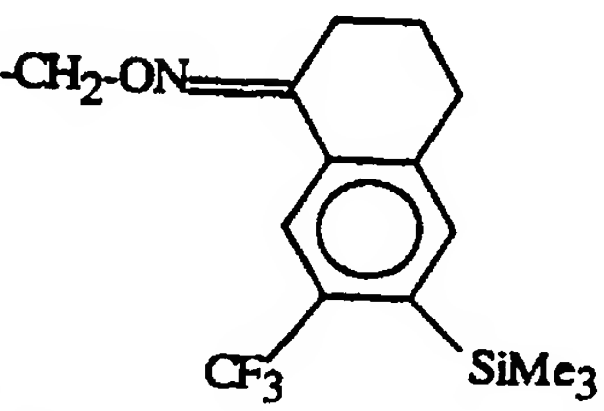
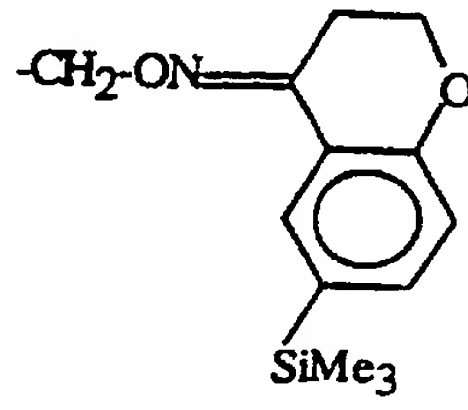
Y-Z	Y-Z	Y-Z
		
		
		

Table 61

Compounds of Formula I wherein: $E = E^5$, $R^1 = \text{Me}$, $R^5 = \text{Me}$, $s = 0$, and

Y-Z	Y-Z	Y-Z
		
		

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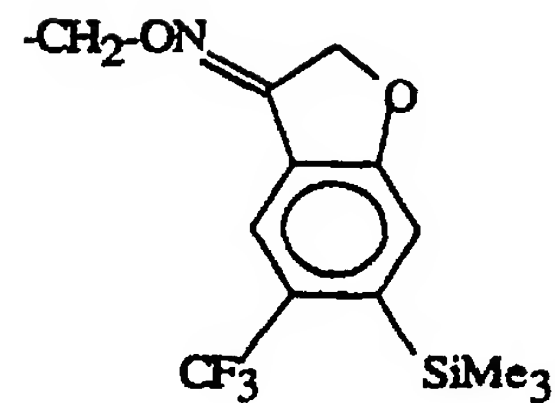
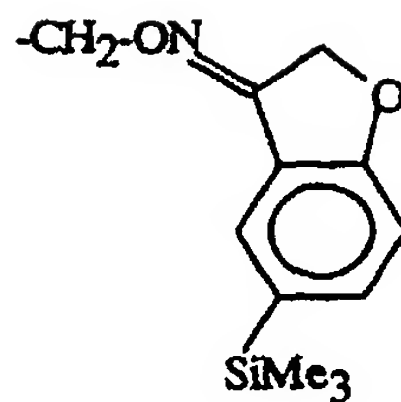
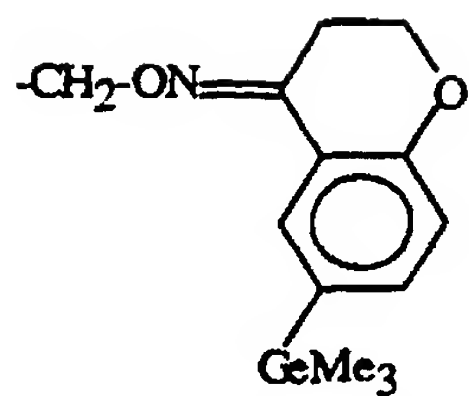
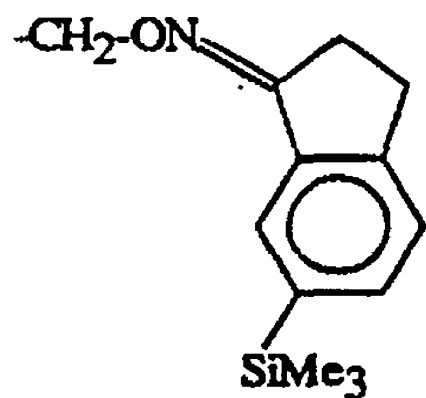
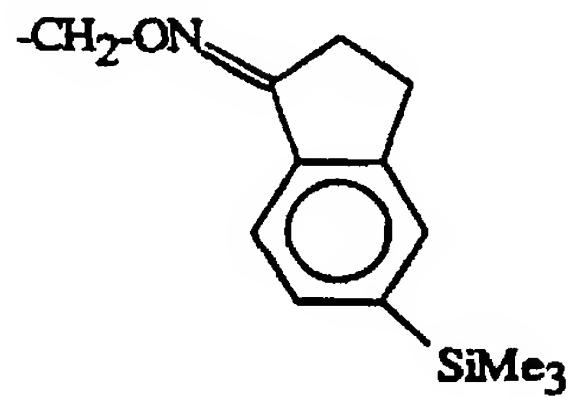
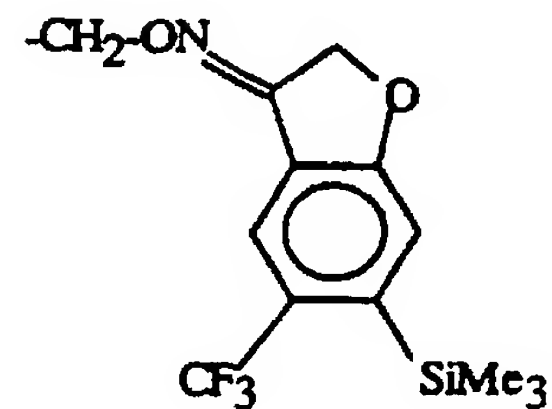
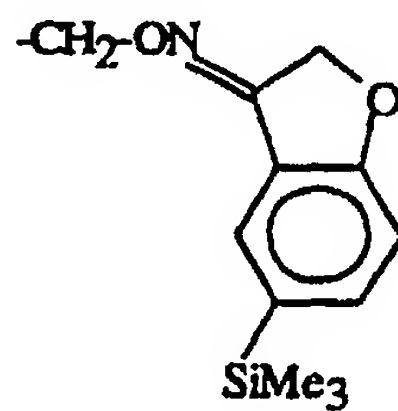
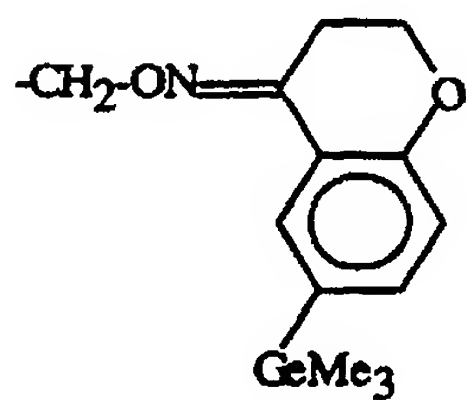
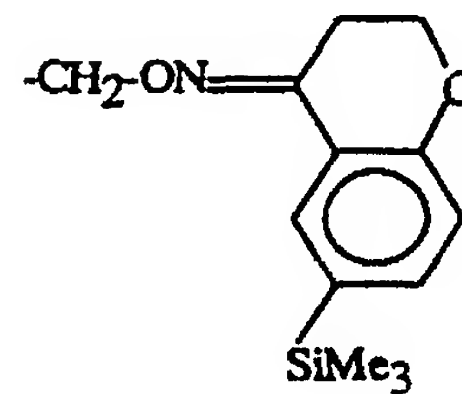
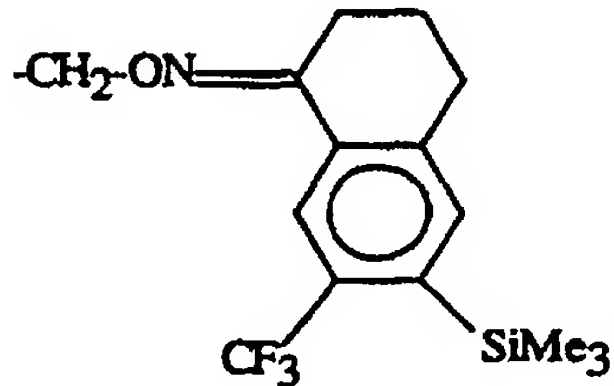
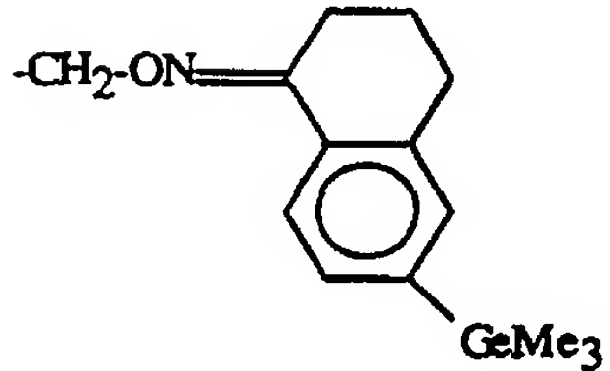
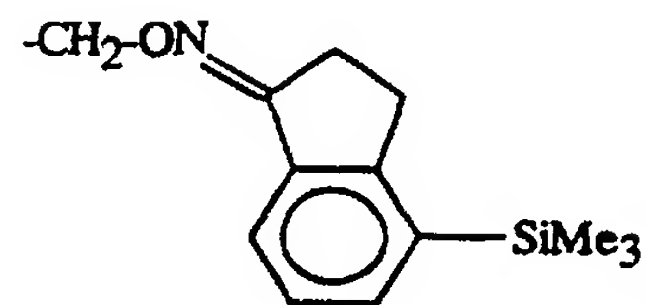


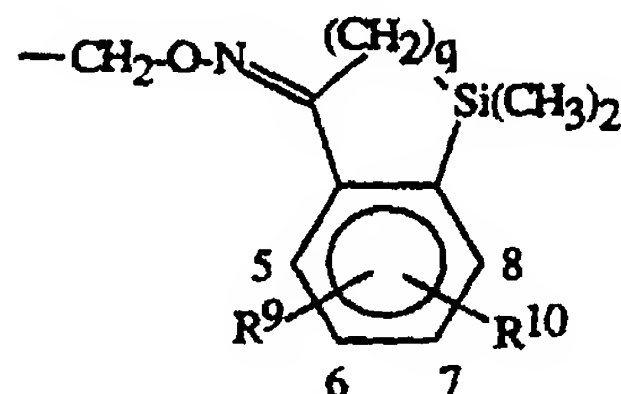
Table 62

Compounds of Formula I wherein: $\text{E} = \text{E}^6$, $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{H}$, $\text{R}^5 = \text{Me}$, $s = 0$, andY-ZY-ZY-Z

84

Table 63

Compounds of Formula I wherein: $E = E^1$, $G = C$, $W = O$, $X = OMe$, $A = O$, $R^{10} = H$, $R^2 = Me$, R^3 and $R^4 = H$, the floating double bond is attached to G and, Y and Z taken together form:

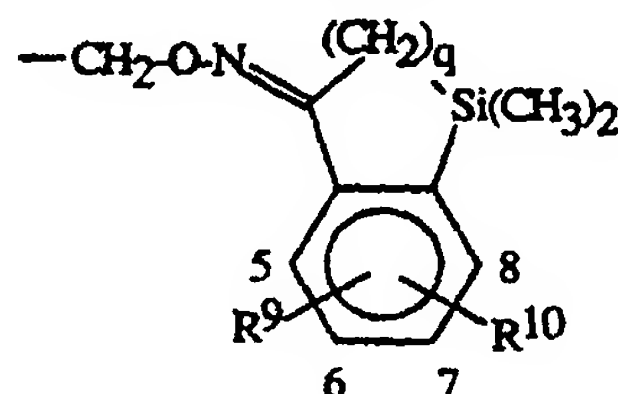


5

R^9	q	R^9	q
H	1	7-CH ₃	1
H	2	6-CH ₃	2
6-CF ₃	1	6-Cl	1
6-CF ₃	2	7-Cl	2

Table 64

Compounds of Formula I wherein: $E = E^1$, $G = N$, $W = O$, $A = N$, $X = OMe$, $R^{10} = H$, $R^2 = Me$, R^3 and $R^4 = H$, the floating double bond is attached to A and, Y and Z taken together form:

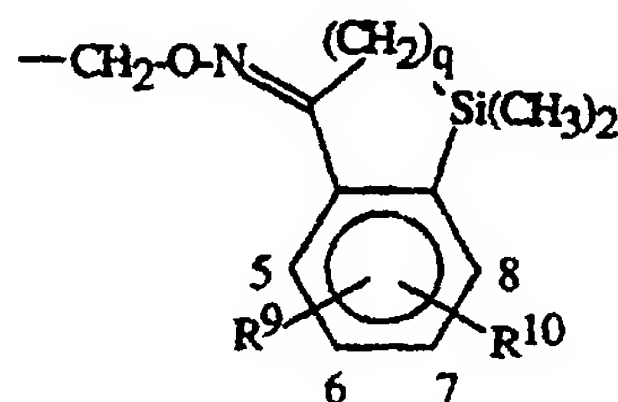


10

R^9	q	R^9	q
H	1	7-CH ₃	1
H	2	6-CH ₃	2
6-CF ₃	1	6-Cl	1
6-CF ₃	2	7-Cl	2

Table 65

Compounds of Formula I wherein: $E = E^2$, $R^1 = Me$, $R^5 = Me$, $R^{10} = H$, and Y and Z taken together form:



15

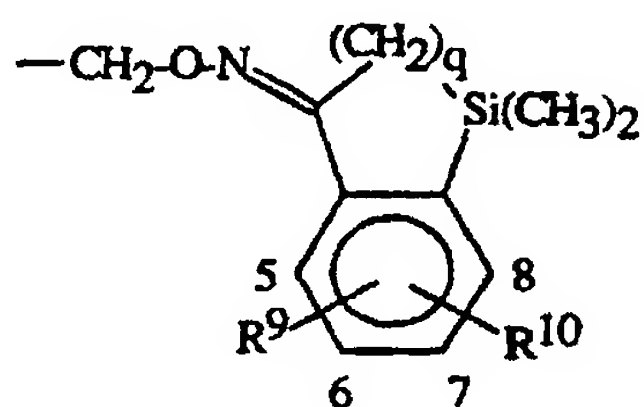
R^9	q	R^9	q
H	1	7-CH ₃	1

85

H	2	6-CH ₃	2
6-CF ₃	1	6-Cl	1
6-CF ₃	2	7-Cl	2

Table 66

Compounds of Formula I wherein: $E = E^3$, $R^1 = \text{Me}$, $R^5 = \text{Me}$, $R^{10} = \text{H}$, and Y and Z taken together form:



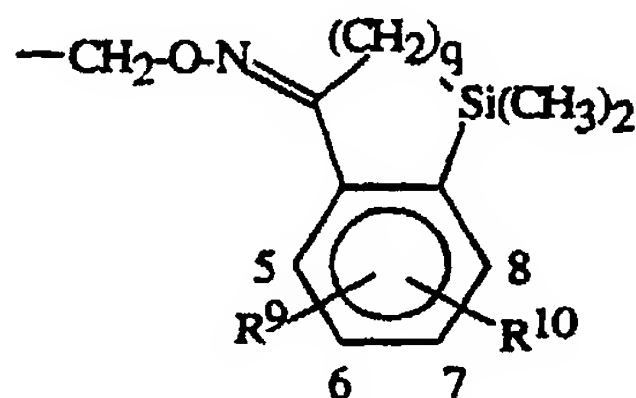
5

R^9	q	R^9	q
H	1	7-CH ₃	1
H	2	6-CH ₃	2
6-CF ₃	1	6-Cl	1
6-CF ₃	2	7-Cl	2

Table 67

Compounds of Formula I wherein: $E = E^4$, $R^1 = \text{Me}$, $R^2 = \text{H}$, $R^5 = \text{Me}$, $R^{10} = \text{H}$, and Y and Z taken together form:

10

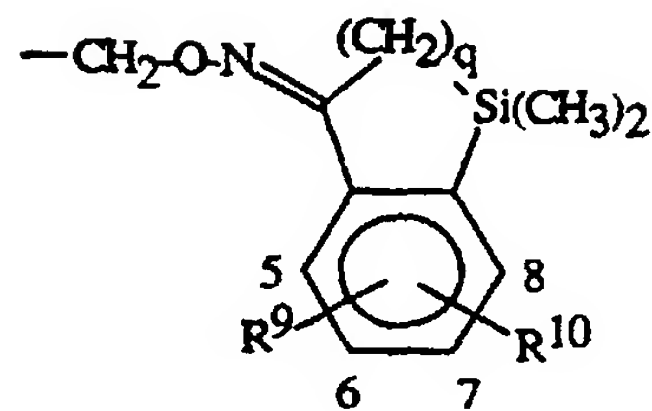


R^9	q	R^9	q
H	1	7-CH ₃	1
H	2	6-CH ₃	2
6-CF ₃	1	6-Cl	1
6-CF ₃	2	7-Cl	2

86

Table 68

Compounds of Formula I wherein: $E = E^5$, $R^1 = \text{Me}$, $R^5 = \text{Me}$, $R^{10} = \text{H}$, $s = 0$, and Y and Z taken together form:

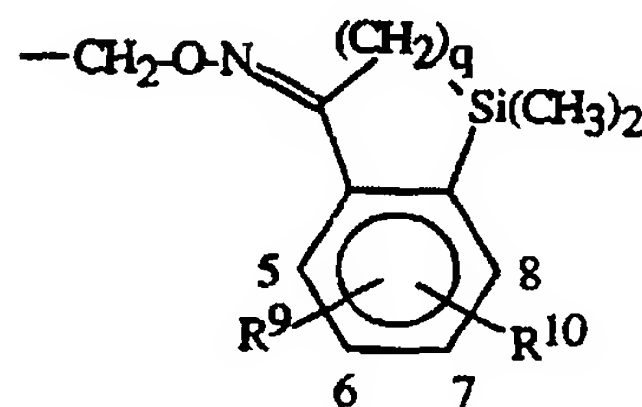


5

R^9	q	R^9	q
H	1	7-CH ₃	1
H	2	6-CH ₃	2
6-CF ₃	1	6-Cl	1
6-CF ₃	2	7-Cl	2

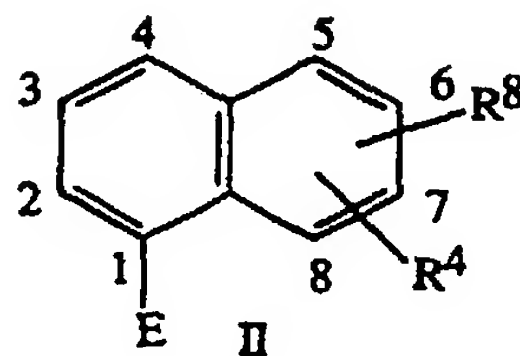
Table 69

Compounds of Formula I wherein: $E = E^6$, $R^1 = \text{Me}$, $R^2 = \text{H}$, $R^5 = \text{Me}$, $R^{10} = \text{H}$, $s = 0$, and Y and Z taken together form:



10

R^9	q	R^9	q
H	1	7-CH ₃	1
H	2	6-CH ₃	2
6-CF ₃	1	6-Cl	1
6-CF ₃	2	7-Cl	2



(Formula I wherein R^3 , Y, and Z are taken together with the phenyl ring to form a naphthalene moiety substituted on either ring with R^8 and on either ring with R^4)

Table 70

Structure of Formula II wherein: $E = E^1$, $R^2 = \text{Me}$, $G = \text{C}$, $W = \text{O}$, $X = \text{OMe}$, $A = \text{O}$ and the floating double bond is attached to G and

R^8	R^4	R^8	R^4
7-SiMe ₃	H	7-SiMe ₃	3-Cl
6-SiMe ₃	H	3-SiMe ₃	7-Ph
7-GeMe ₃	H	3-SiMe ₃	7-Me
6-GeMe ₃	H	7-SiMe ₃	3-Me

Table 71

Formula II wherein: $E = E^1$, $G = \text{N}$, $W = \text{O}$, $A = \text{N}$, $X = \text{OMe}$, $R^2 = \text{Me}$ and the floating double bond is attached to A and

R^8	R^4	R^8	R^4
7-SiMe ₃	H	7-SiMe ₃	3-Cl
6-SiMe ₃	H	3-SiMe ₃	7-Ph
7-GeMe ₃	H	3-SiMe ₃	7-Me
6-GeMe ₃	H	7-SiMe ₃	3-Me

5

Table 72

Formula II wherein: $E = E^2$, $R^1 = \text{Me}$, $R^5 = \text{Me}$, and

R^8	R^4	R^8	R^4
7-SiMe ₃	H	7-SiMe ₃	3-Cl
6-SiMe ₃	H	3-SiMe ₃	7-Ph
7-GeMe ₃	H	3-SiMe ₃	7-Me
6-GeMe ₃	H	7-SiMe ₃	3-Me

Table 73

Formula II wherein: $E = E^3$, $R^1 = \text{Me}$, $R^5 = \text{Me}$, and

R^8	R^4	R^8	R^4
7-SiMe ₃	H	7-SiMe ₃	3-Cl
6-SiMe ₃	H	3-SiMe ₃	7-Ph
7-GeMe ₃	H	3-SiMe ₃	7-Me
6-GeMe ₃	H	7-SiMe ₃	3-Me

Table 74

Formula II wherein: $E = E^4$, $R^1 = \text{Me}$, $R^2 = \text{H}$, $R^5 = \text{Me}$, and

R^8	R^4	R^8	R^4
7-SiMe ₃	H	7-SiMe ₃	3-Cl
6-SiMe ₃	H	3-SiMe ₃	7-Ph
7-GeMe ₃	H	3-SiMe ₃	7-Me

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6-GeMe ₃	H	7-SiMe ₃	3-Me
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Table 75

Formula II wherein: E = E⁵, R¹ = Me, R⁵ = Me, s = 0, and

<u>R</u> ⁸	<u>R</u> ⁴	<u>R</u> ⁸	<u>R</u> ⁴
7-SiMe ₃	H	7-SiMe ₃	3-Cl
6-SiMe ₃	H	3-SiMe ₃	7-Ph
7-GeMe ₃	H	3-SiMe ₃	7-Me
6-GeMe ₃	H	7-SiMe ₃	3-Me

Table 76

Formula II wherein: E = E⁶, R¹ = Me, R² = H, R⁵ = Me, s = 0, and

<u>R</u> ⁸	<u>R</u> ⁴	<u>R</u> ⁸	<u>R</u> ⁴
7-SiMe ₃	H	7-SiMe ₃	3-Cl
6-SiMe ₃	H	3-SiMe ₃	7-Ph
7-GeMe ₃	H	3-SiMe ₃	7-Me
6-GeMe ₃	H	7-SiMe ₃	3-Me

5

Table 77

Compounds of Formula I wherein E = E¹, R³ = R⁴ = H, Y = CH₂ON=C(CH₃),
Z = 3-Me₃Si-Ph andG = C, A = O, the floating double
bond is attached to G and

<u>W</u>	<u>W</u>	<u>W</u>
NH	NEt	NOMe
NMe	NHex	NOEt
		NO- <i>n</i> -Hex

G = N, A = N, the floating double bond is
attached to A and

<u>W</u>	<u>W</u>	<u>W</u>
NH	NEt	NOMe
NMe	NHex	NOEt
		NO- <i>n</i> -Hex

Table 78

Compounds of Formula I wherein E = E¹, R³ = R⁴ = H, Y = CH₂O,Z = 2-Me-5-Me₃Si-Ph andG = C, A = O, the floating double
bond is attached to G and

<u>W</u>	<u>W</u>	<u>W</u>
NH	NEt	NOMe
NMe	NHex	NOEt
		NO- <i>n</i> -Hex

G = N, A = N, the floating double bond is
attached to A and

<u>W</u>	<u>W</u>	<u>W</u>
NH	NEt	NOMe
NMe	NHex	NOEt
		NO- <i>n</i> -Hex

Table 79

Compounds of Formula I wherein $E = E^1$, $G = C$, $W = O$, $R^3 = R^4 = H$,

$A = O$, $X = OMe$, and the double bond is attached to G

$Y = CH_2O$, $Z = 2-Me-5-Me_3Si-Ph$ and		$Y = CH_2ON=C(CH_3)$, $Z = 3-Me_3Si-Ph$ and	
R^2	R^2	R^2	R^2
OH	CH_2CF_3	OH	CH_2CF_3
OMe	$CH_2CH=CH_2$	OMe	$CH_2CH=CH_2$
OEt	$CH_2C=CH$	OEt	$CH_2C=CH$
OCOMe	COMe	OCOMe	COMe
	COOMe		COOMe

Compounds of Formula I wherein $E = E^1$, $G = N$, $W = O$, $R^3 = R^4 = H$,

$A = N$, $X = OMe$, the double bond is attached to A and

$Y = CH_2O$, $Z = 2-Me-5-Me_3Si-Ph$ and		$Y = CH_2ON=C(CH_3)$, $Z = 3-Me_3Si-Ph$ and	
R^2	R^2	R^2	R^2
OH	CH_2CF_3	OH	CH_2CF_3
OMe	$CH_2CH=CH_2$	OMe	$CH_2CH=CH_2$
OEt	$CH_2C=CH$	OEt	$CH_2C=CH$
OCOMe	COMe	OCOMe	COMe
	COOMe		COOMe

Formulation/Utility

- 5 Compounds of this invention will generally be used as a formulation or composition with an agriculturally suitable carrier comprising at least one of a liquid diluent, a solid diluent or a surfactant. The formulation or composition ingredients are selected to be consistent with the physical properties of the active ingredient, mode of application and environmental factors such as soil type, moisture and temperature.
- 10 Useful formulations include liquids such as solutions (including emulsifiable concentrates), suspensions, emulsions (including microemulsions and/or suspoemulsions) and the like which optionally can be thickened into gels. Useful formulations further include solids such as dusts, powders, granules, pellets, tablets, films, and the like which can be water-dispersible ("wetttable") or water-soluble. Active ingredient can be
- 15 (micro)encapsulated and further formed into a suspension or solid formulation; alternatively the entire formulation of active ingredient can be encapsulated (or "overcoated"). Encapsulation can control or delay release of the active ingredient. Sprayable formulations can be extended in suitable media and used at spray volumes from about one to several hundred liters per hectare. High-strength compositions are
- 20 primarily used as intermediates for further formulation.

The formulations will typically contain effective amounts of active ingredient, diluent and surfactant within the following approximate ranges which add up to 100 percent by weight.

	Weight Percent		
	<u>Active Ingredient</u>	<u>Diluent</u>	<u>Surfactant</u>
Water-Dispersible and Water-soluble Granules, Tablets and Powders.	5-90	0-94	1-15
Suspensions, Emulsions, Solutions (including Emulsifiable Concentrates)	5-50	40-95	0-15
Dusts	1-25	70-99	0-5
Granules and Pellets	0.01-99	5-99.99	0-15
High Strength Compositions	90-99	0-10	0-2

Typical solid diluents are described in Watkins, et al., *Handbook of Insecticide Dust Diluents and Carriers*, 2nd Ed., Dorland Books, Caldwell, New Jersey. Typical liquid diluents are described in Marsden, *Solvents Guide*, 2nd Ed., Interscience, New York, 1950. *McCutcheon's Detergents and Emulsifiers Annual*, Allured Publ. Corp., Ridgewood, New Jersey, as well as Sisely and Wood, *Encyclopedia of Surface Active Agents*, Chemical Publ. Co., Inc., New York, 1964, list surfactants and recommended uses. All formulations can contain minor amounts of additives to reduce foam, caking, corrosion, microbiological growth and the like, or thickeners to increase viscosity.

Surfactants include, for example, polyethoxylated alcohols, polyethoxylated alkylphenols, polyethoxylated sorbitan fatty acid esters, dialkyl sulfosuccinates, alkyl sulfates, alkylbenzene sulfonates, organosilicones, *N,N*-dialkyltaurates, lignin sulfonates, naphthalene sulfonate formaldehyde condensates, polycarboxylates, and polyoxyethylene/polyoxypropylene block copolymers. Solid diluents include, for example, clays such as bentonite, montmorillonite, attapulgite and kaolin, starch, sugar, silica, talc, diatomaceous earth, urea, calcium carbonate, sodium carbonate and bicarbonate, and sodium sulfate. Liquid diluents include, for example, water, *N,N*-dimethylformamide, dimethyl sulfoxide, *N*-alkylpyrrolidone, ethylene glycol, polypropylene glycol, paraffins, alkylbenzenes, alkylnaphthalenes, oils of olive, castor, linseed, tung, sesame, corn, peanut, cotton-seed, soybean, rape-seed and coconut, fatty acid esters, ketones such as cyclohexanone, 2-heptanone, isophorone and 4-hydroxy-4-methyl-2-pentanone, and alcohols such as methanol, cyclohexanol, decanol and tetrahydrofurfuryl alcohol.

Solutions, including emulsifiable concentrates, can be prepared by simply mixing the ingredients. Dusts and powders can be prepared by blending and, usually, grinding as

in a hammer mill or fluid-energy mill. Suspensions are usually prepared by wet-milling; see, for example, U.S. 3,060,084. Granules and pellets can be prepared by spraying the active material upon preformed granular carriers or by agglomeration techniques. See Browning, "Agglomeration", *Chemical Engineering*, December 4, 1967, pp 147-48, 5 *Perry's Chemical Engineer's Handbook*, 4th Ed., McGraw-Hill, New York, 1963, pages 8-57 and following, and WO 91/13546. Pellets can be prepared as described in U.S. 4,172,714. Water-dispersible and water-soluble granules can be prepared as taught in U.S. 4,144,050, U.S. 3,920,442 and DE 3,246,493. Tablets can be prepared as taught in U.S. 5,180,587, U.S. 5,232,701 and U.S. 5,208,030. Films can be prepared as taught 10 in GB 2,095,558 and U.S. 3,299,566.

For further information regarding the art of formulation, see U.S. 3,235,361, Col. 6, line 16 through Col. 7, line 19 and Examples 10-41; U.S. 3,309,192, Col. 5, line 43 through Col. 7, line 62 and Examples 8, 12, 15, 39, 41, 52, 53, 58, 132, 138-140, 162-164, 166, 167 and 169-182; U.S. 2,891,855, Col. 3, line 66 through Col. 5, line 17 15 and Examples 1-4; Klingman, *Weed Control as a Science*, John Wiley and Sons, Inc., New York, 1961, pp 81-96; and Hance et al., *Weed Control Handbook*, 8th Ed., Blackwell Scientific Publications, Oxford, 1989.

In the following Examples, all percentages are by weight and all formulations are prepared in conventional ways. Compound numbers refer to compounds in Index 20 Tables A-E.

Example A

Wettable Powder

	Compound 15	65.0%
	dodecylphenol polyethylene glycol ether	2.0%
25	sodium ligninsulfonate	4.0%
	sodium silicoaluminate	6.0%
	montmorillonite (calcined)	23.0%.

Example B

Granule

30	Compound 15	10.0%
	attapulgit granules (low volatile matter, 0.71/0.30 mm; U.S.S. No. 25-50 sieves)	90.0%.

Example CExtruded Pellet

	Compound 15	25.0%
	anhydrous sodium sulfate	10.0%
5	crude calcium ligninsulfonate	5.0%
	sodium alkyl naphthalenesulfonate	1.0%
	calcium/magnesium bentonite	59.0%.

Example DEmulsifiable Concentrate

10	Compound 15	20.0%
	blend of oil soluble sulfonates and polyoxyethylene ethers	10.0%
	isophorone	70.0%.

The compounds of this invention are useful as plant disease control agents. The present invention therefore further comprises a method for controlling plant diseases caused by fungal plant pathogens comprising applying to the plant or portion thereof to be protected, or to the plant seed or seedling to be protected, an effective amount of a compound of the invention or a fungicidal composition containing said compound. The compounds and compositions of this invention provide control of diseases caused by a broad spectrum of fungal plant pathogens in the Basidiomycete, Ascomycete, Oomycete and Deuteromycete classes. They are effective in controlling a broad spectrum of plant diseases, particularly foliar pathogens of ornamental, vegetable, field, cereal, and fruit crops. These pathogens include *Plasmopara viticola*, *Phytophthora infestans*, *Peronospora tabacina*, *Pseudoperonospora cubensis*, *Pythium aphanidermatum*, *Alternaria brassicae*, *Septoria nodorum*, *Septoria tritici*, *Cercosporidium personatum*, *Cercospora arachidicola*, *Pseudocercospora herpotrichoides*, *Cercospora beticola*, *Botrytis cinerea*, *Monilinia fructicola*, *Pyricularia oryzae*, *Podosphaera leucotricha*, *Venturia inaequalis*, *Erysiphe graminis*, *Uncinula necator*, *Puccinia recondita*, *Puccinia graminis*, *Hemileia vastatrix*, *Puccinia striiformis*, *Puccinia arachidis*, *Rhizoctonia solani*, *Sphaerotheca fuliginea*, *Fusarium oxysporum*, *Verticillium dahliae*, *Pythium aphanidermatum*, *Phytophthora megasperma*, *Sclerotinia sclerotiorum*, *Sclerotium rolfsii*, *Erysiphe polygoni*, *Pyrenophora teres*, *Gaeumannomyces graminis*, *Rhynchosporium secalis*, *Fusarium roseum*, *Bremia lactucae* and other genera and species closely related to these pathogens.

The compounds of this invention also exhibit activity against a wide spectrum of foliar-feeding, fruit-feeding, stem or root feeding, seed-feeding, aquatic and soil-inhabiting arthropods (term "arthropods" includes insects, mites and nematodes) which are pests of growing and stored agronomic crops, forestry, greenhouse crops,

ornamentals, nursery crops, stored food and fiber products, livestock, household, and public and animal health. Those skilled in the art will appreciate that not all compounds are equally effective against all growth stages of all pests. Nevertheless, all of the compounds of this invention display activity against pests that include: eggs, larvae and adults of the Order Lepidoptera; eggs, foliar-feeding, fruit-feeding, root-feeding, seed-feeding larvae and adults of the Order Coleoptera; eggs, immatures and adults of the Orders Hemiptera and Homoptera; eggs, larvae, nymphs and adults of the Order Acari; eggs, immatures and adults of the Orders Thysanoptera, Orthoptera and Dermaptera; eggs, immatures and adults of the Order Diptera; and eggs, juveniles and adults of the Phylum Nematoda. The compounds of this invention are also active against pests of the Orders Hymenoptera, Isoptera, Siphonaptera, Blattaria, Thysanura and Psocoptera; pests belonging to the Class Arachnida and Phylum Platyhelminthes. Specifically, the compounds are active against southern corn rootworm (*Diabrotica undecimpunctata howardi*), aster leafhopper (*Mascrostes fascifrons*), boll weevil (*Anthonomus grandis*), two-spotted spider mite (*Tetranychus urticae*), fall armyworm (*Spodoptera frugiperda*), black bean aphid (*Aphis fabae*), green peach aphid (*Myzus persica*), cotton aphid (*Aphis gossypii*), Russian wheat aphid (*Diuraphis noxia*), English grain aphid (*Sitobion avenae*), tobacco budworm (*Heliothis virescens*), rice water weevil (*Lissorhoptrus oryzophilus*), rice leaf beetle (*Oulema oryzae*), whitebacked planthopper (*Sogatella furcifera*), green leafhopper (*Nephotettix cincticeps*), brown planthopper (*Nilaparvata lugens*), small brown planthopper (*Laodelphax striatellus*), rice stem borer (*Chilo suppressalis*), rice leafroller (*Cnaphalocrocis medinalis*), black rice stink bug (*Scotinophara lurida*), rice stink bug (*Oebalus pugnax*), rice bug (*Leptocorisa chinensis*), slender rice bug (*Cletus puntiger*), and southern green stink bug (*Nezara viridula*). The compounds are active on mites, demonstrating ovicidal, larvicidal and chemosterilant activity against such families as Tetranychidae including *Tetranychus urticae*, *Tetranychus cinnabarinus*, *Tetranychus mcdanieli*, *Tetranychus pacificus*, *Tetranychus turkestanii*, *Byrobia rubrioculus*, *Panonychus ulmi*, *Panonychus citri*, *Eotetranychus carpini borealis*, *Eotetranychus hicoriae*, *Eotetranychus sexmaculatus*, *Eotetranychus yumensis*, *Eotetranychus banksi* and *Oligonychus pratensis*; Tenuipalpidae including *Brevipalpus lewisi*, *Brevipalpus phoenicis*, *Brevipalpus californicus* and *Brevipalpus obovatus*; Eriophyidae including *Phyllocoptruta oleivora*, *Eriophyes sheldoni*, *Aculus cornutus*, *Epitrimerus pyri* and *Eriophyes mangiferae*. See WO 90/10623 and WO 92/00673 for more detailed pest descriptions.

Compounds of this invention can also be mixed with one or more other insecticides, fungicides, nematocides, bactericides, acaricides, growth regulators, chemosterilants, semiochemicals, repellents, attractants, pheromones, feeding stimulants or other biologically active compounds to form a multi-component pesticide giving an

even broader spectrum of agricultural protection. Examples of such agricultural protectants with which compounds of this invention can be formulated are: insecticides such as abamectin, acephate, azinphos-methyl, bifenthrin, buprofezin, carbofuran, chlorpyrifos, chlorpyrifos-methyl, cyfluthrin, beta-cyfluthrin, deltamethrin, diafenthiuron, diazinon, diflubenzuron, dimethoate, esfenvalerate, fenpropathrin, fenvalerate, fipronil, flucythrinate, tau-fluvalinate, fonophos, imidacloprid, isofenphos, malathion, metaldehyde, methamidophos, methidathion, methomyl, methoprene, methoxychlor, monocrotophos, oxamyl, parathion, parathion-methyl, permethrin, phorate, phosalone, phosmet, phosphamidon, pirimicarb, profenofos, rotenone, sulprofos, tebufenozide, tefluthrin, terbufos, tetrachlorvinphos, thiodicarb, tralomethrin, trichlorfon and triflumuron; fungicides such as azoxystrobin (ICIA5504), benomyl, blastidicid-S, Bordeaux mixture (tribasic copper sulfate), bromuconazole, captafol, captan, carbendazim, chloroneb, chlorothalonil, copper oxychloride, copper salts, cymoxanil, cyproconazole, cyprodinil (CGA 219417), diclomezine, dicloran, difenoconazole, dimethomorph, diniconazole, diniconazole-M, dodine, edifenphos, epoxyconazole (BAS 480F), fenarimol, fenbuconazole, fenciclonil, fenpropidin, fenpropimorph, fluquinconazole, flusilazole, flutolanil, flutriafol, folpet, fosetyl-aluminum, furalaxyl, hexaconazole, ipconazole, iprobenfos, iprodione, isoprothiolane, kasugamycin, kresoxim-methyl (BAS 490F), mancozeb, maneb, mepronil, metalaxyl, metconazole, myclobutanil, neo-asozin (ferric methanearsonate), oxadixyl, penconazole, pencycuron, probenazole, prochloraz, propiconazole, pyrifenox, pyroquilon, sulfur, tebuconazole, tetraconazole, thiabendazole, thiophanate-methyl, thiram, triadimefon, triadimenol, tricyclazole, triticonazole, uniconazole, validamycin and vinclozolin; nematocides such as aldoxycarb and fenamiphos; bactericides such as streptomycin; acaricides such as amitraz, chinomethionat, chlorobenzilate, cyhexatin, dicofol, dienochlor, fenazaquin, fenbutatin oxide, fenpropathrin, fenpyroximate, hexythiazox, propargite, pyridaben and tebufenpyrad; and biological agents such as *Bacillus thuringiensis*, *Bacillus thuringiensis* delta endotoxin, baculovirus, and entomopathogenic bacteria, virus and fungi.

In certain instances, combinations with other fungicides or arthropodicides having a similar spectrum of control but a different mode of action will be particularly advantageous for resistance management.

Preferred are mixtures of a compound of the invention with a fungicide selected from the group cyproconazole, cyprodinil (CGA 219417), epoxyconazole (BAS 480F), fenpropidin, fenpropimorph, flusilazole and tebuconazole. Specifically preferred mixtures (compound numbers refer to compounds in Index Tables A-E) are selected from the group: compound 2 and cyproconazole; compound 2 and cyprodinil (CGA 219417); compound 2 and epoxyconazole (BAS 480F); compound 2 and fenpropidin; compound 2 and fenpropimorph; compound 2 and flusilazole; compound 2

and tebuconazole; compound 15 and cyproconazole; compound 15 and cyprodinil (CGA 219417); compound 15 and epoxyconazole (BAS 480F); compound 15 and fenpropidin; compound 15 and fenpropimorph; compound 15 and flusilazole; compound 15 and tebuconazole; compound 16 and cyproconazole; compound 16 and cyprodinil (CGA 219417); compound 16 and epoxyconazole (BAS 480F); compound 16 and fenpropidin; compound 16 and fenpropimorph; compound 16 and flusilazole; compound 16 and tebuconazole; compound 20 and cyproconazole; compound 20 and cyprodinil (CGA 219417); compound 20 and epoxyconazole (BAS 480F); compound 20 and fenpropidin; compound 20 and fenpropimorph; compound 20 and flusilazole; compound 20 and tebuconazole; compound 23 and cyproconazole; compound 23 and cyprodinil (CGA 219417); compound 23 and epoxyconazole (BAS 480F); compound 23 and fenpropidin; compound 23 and fenpropimorph; compound 23 and flusilazole; and compound 23 and tebuconazole.

Plant disease control is ordinarily accomplished by applying an effective amount of a compound of this invention either pre- or post-infection, to the portion of the plant to be protected such as the roots, stems, foliage, fruit, seeds, tubers or bulbs, or to the media (soil or sand) in which the plants to be protected are growing. The compounds can also be applied to the seed to protect the seed and seedling.

For plant disease control, rates of application for these compounds can be influenced by many factors of the environment and should be determined under actual use conditions. Foliage can normally be protected when treated at a rate of from less than 1 g/ha to 5,000 g/ha of active ingredient. Seed and seedlings can normally be protected when seed is treated at a rate of from 0.1 to 10 g per kilogram of seed.

Arthropod pests are controlled and protection of agronomic, horticultural and specialty crops, animal and human health is achieved by applying one or more of the compounds of this invention, in an effective amount, to the environment of the pests including the agronomic and/or nonagronomic locus of infestation, to the area to be protected, or directly on the pests to be controlled. Thus, the present invention further comprises a method for the control of foliar and soil inhabiting arthropods and nematode pests and protection of agronomic and/or nonagronomic crops, comprising applying one or more of the compounds of the invention, or compositions containing at least one such compound, in an effective amount, to the environment of the pests including the agronomic and/or nonagronomic locus of infestation, to the area to be protected, or directly on the pests to be controlled. A preferred method of application is by spraying. Alternatively, granular formulations of these compounds can be applied to the plant foliage or the soil. Other methods of application include direct and residual sprays, aerial sprays, seed coats, microencapsulations, systemic uptake, baits, eartags, boluses, foggers, fumigants, aerosols, dusts and many others. The compounds can be

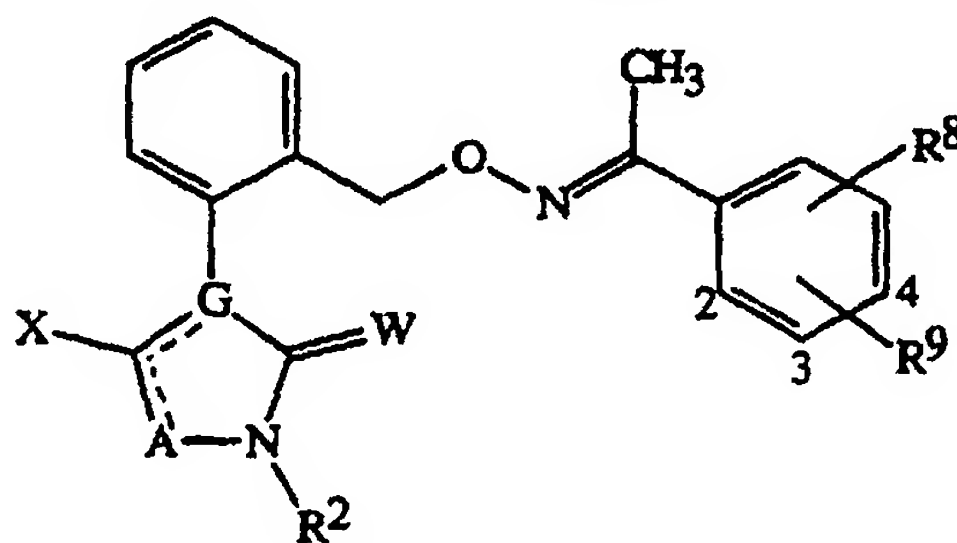
incorporated into baits that are consumed by the arthropods or in devices such as traps and the like.

For the control arthropod pests, the compounds of this invention can be applied in their pure state, but most often application will be of a formulation comprising one or more compounds with suitable carriers, diluents, and surfactants and possibly in combination with a food depending on the contemplated end use. A preferred method of application involves spraying a water dispersion or refined oil solution of the compounds. Combinations with spray oils, spray oil concentrations, spreader stickers, adjuvants, other solvents, and synergists such as piperonyl butoxide often enhance compound efficacy.

The rate of application required for effective control will depend on such factors as the species of arthropod to be controlled, the pest's life cycle, life stage, its size, location, time of year, host crop or animal, feeding behavior, mating behavior, ambient moisture, temperature, and the like. Under normal circumstances, application rates of about 0.01 to 2 kg of active ingredient per hectare are sufficient to control pests in agronomic ecosystems, but as little as 0.001 kg/hectare may be sufficient or as much as 8 kg hectare may be required. For nonagronomic applications, effective use rates will range from about 1.0 to 50 mg/square meter but as little as 0.1 mg/square meter may be sufficient or as much as 150 mg/square meter may be required.

The following TESTS demonstrate the control efficacy of compounds of this invention on specific pathogens and arthropod pests. For the tests on arthropod pests, "control efficacy" represents inhibition of arthropod development (including mortality) that causes significantly reduced feeding. The pathogen and arthropod pest control protection afforded by the compounds is not limited, however, to these species. See Index Tables A-E for compound descriptions.

INDEX TABLE A



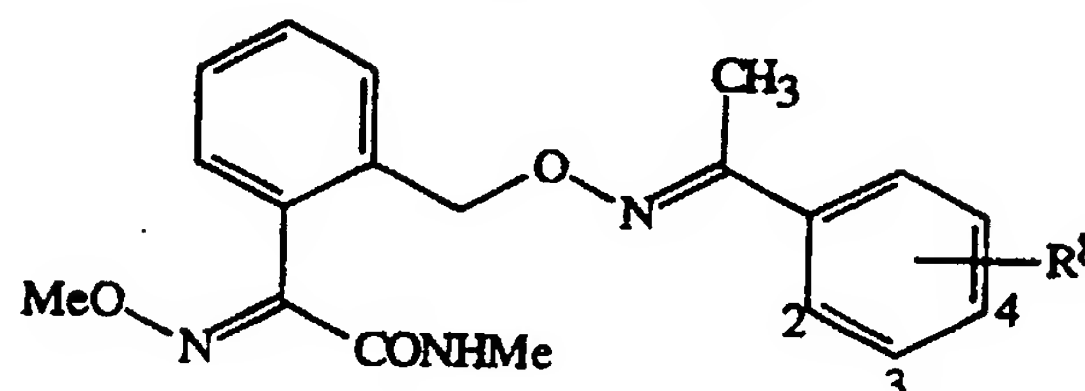
Compound	G	A	W	X	R ²	R ⁸	R ⁹	m.p. (°C)
1 (Ex. 1)	C	O	O	MeO	Me	3-SiMe ₃	H	oil*
2 (Ex. 2)	N	N	O	MeO	Me	3-SiMe ₃	H	72-74

3	N	N	O	Cl	Me	3-SiMe ₃	H	oil*
4	N	N	O	MeO	Me	3-GeMe ₃	H	oil*
5	C	O	O	MeO	Me	3-SiMe ₃	5-SiMe ₃	oil*
6	N	N	O	MeO	Me	3-SiMe ₃	5-SiMe ₃	oil*

*See Index Table E for ¹H NMR data.

INDEX TABLE B

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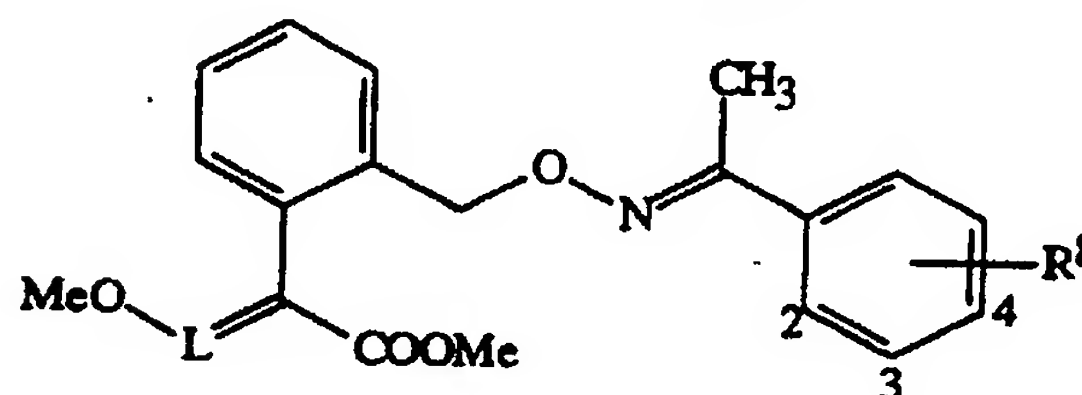


Compound	R ⁸	m.p. (°C)
7 (Ex. 3)	3-SiMe ₃	oil*
8	4-SiMe ₃	115-7
9	3-GeMe ₃	oil*
10	3-SiMe ₂ Ph	oil*
11	3-SiMe ₂ Et	oil*

10

*See Index Table E for ¹H NMR data.

INDEX TABLE C



wherein L is N or CH

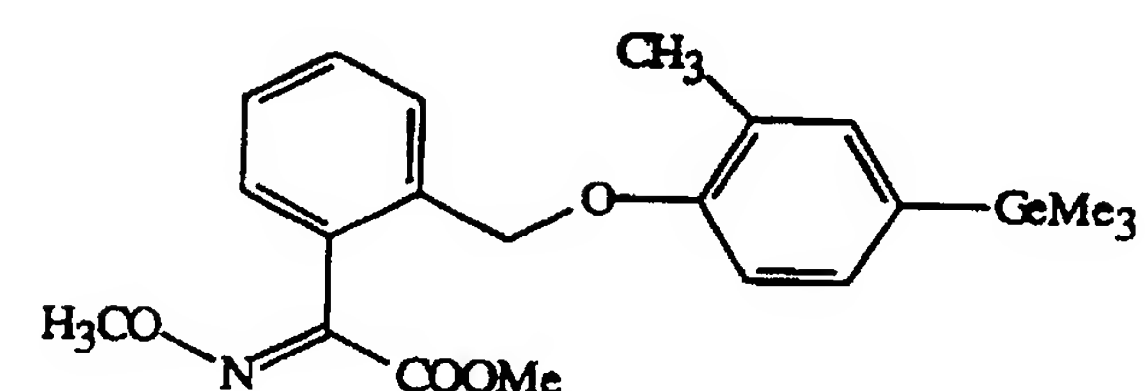
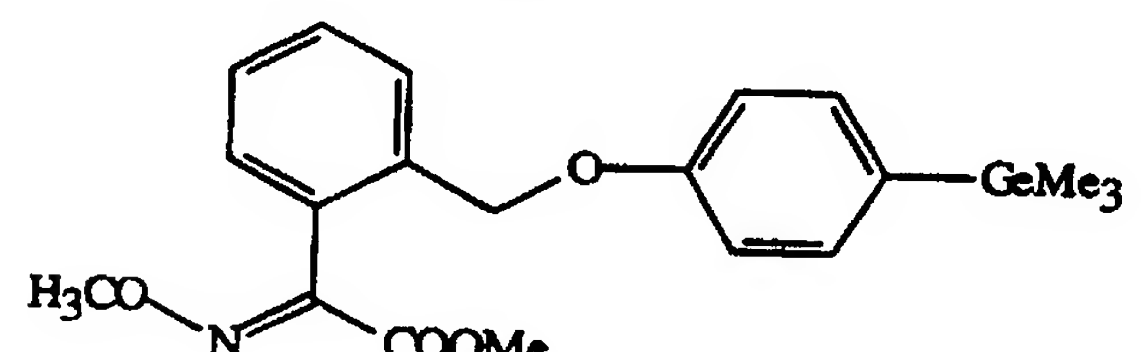
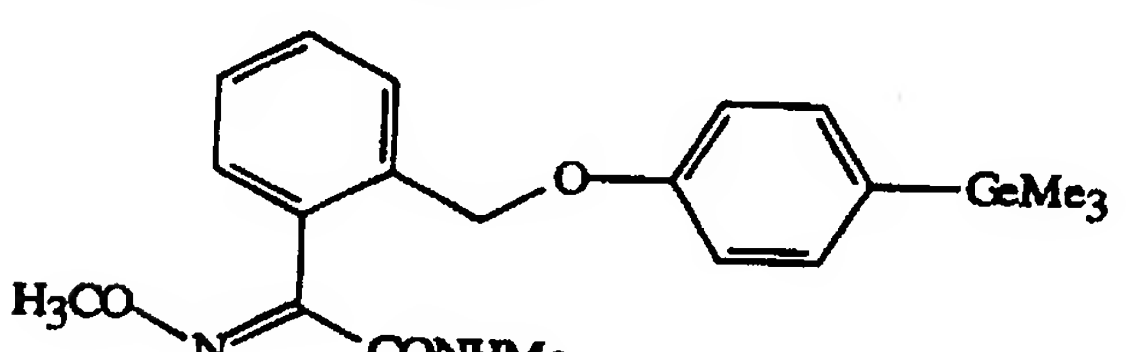
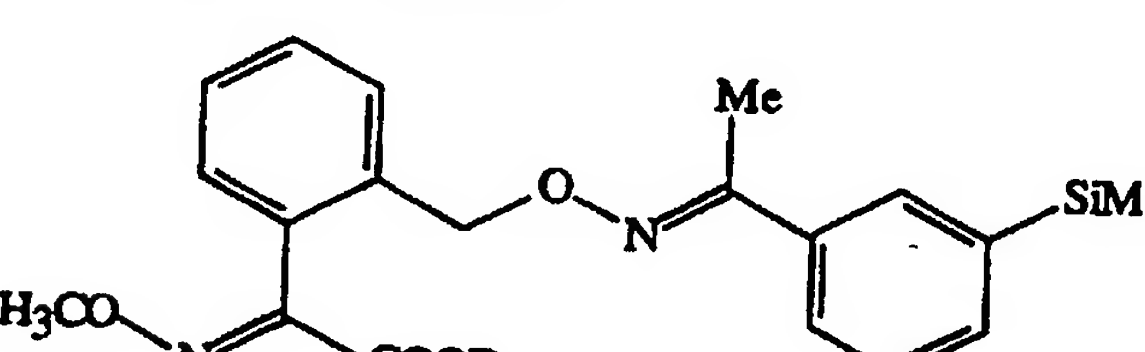
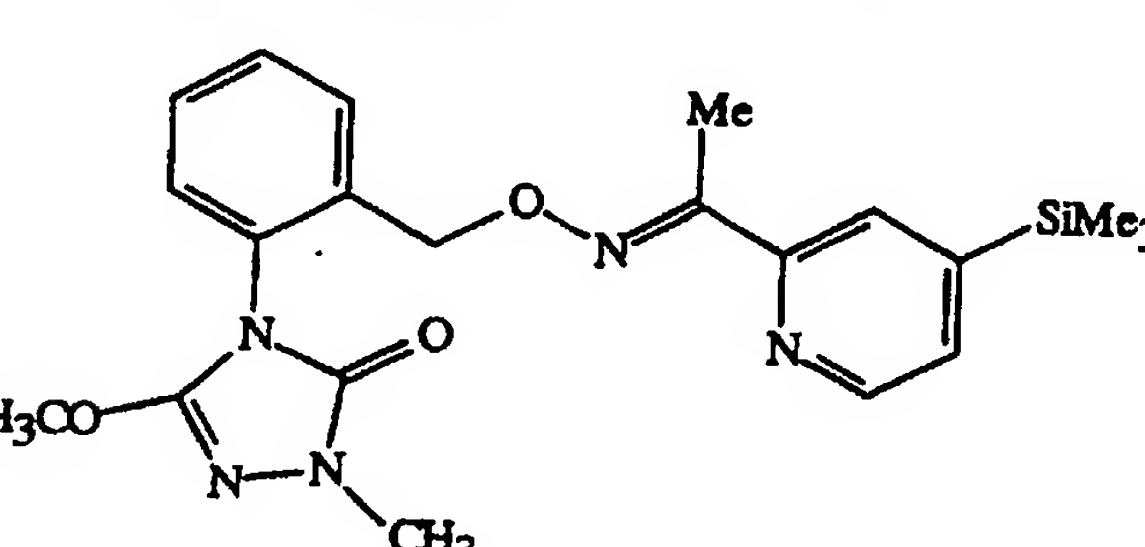
Compound	L	R ⁸	m.p. (°C)
12 (Ex. 4)	CH	4-GeMe ₃	oil*
13	CH	4-SiMe ₃	oil*
14	CH	3-SiMe ₃	oil*
15 (Ex. 5)	N	3-SiMe ₃	oil*
16	N	3-GeMe ₃	oil*
17	N	3-SiMe ₂ (CH=CH ₂)	oil*
18	N	3-SiMe ₂ Et	oil*

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19	N	3-GeEt ₃	70-71
20	N	3-SiMe ₂ Ph	oil*
21	CH	3-SiMe ₂ Ph	oil*
22	CH	3-GeMe ₃	oil*

*See Index Table E for ¹H NMR data.

INDEX TABLE D

Compound	Structure	m.p.(°C)
23 (Ex. 6)		oil*
24		79-81
25		95-101
26		64-66
27		oil*

*See Index Table E for ¹H NMR data.

INDEX TABLE E

Cmpd No.	¹ H NMR Data (CDCl ₃ solution unless indicated otherwise) ^a
1	δ 7.72 (s,1H), 7.54 (m,3H), 7.34 (m,4H), 5.28 (s,2H), 3.91 (s,3H), 3.42 (s,3H), 2.24 (s,3H), 0.27 (s,9H).
3	δ 7.42-7.30 (m,3H), 7.17 (d,1H), 3.54 (s,3H), 2.22 (s,3H).
4	δ 7.63 (s,1H), 7.58 (m,2H), 7.44 (m,3H), 7.30 (t,1H), 7.25 (m,1H), 5.26 (d,1H), 5.23 (d,1H), 3.88 (s,3H), 3.40 (s,3H), 2.20 (s,3H), 0.39 (s,9H).
5	δ 7.69 (s,2H), 7.63 (m,1H), 7.55 (m,1H), 7.34 (m,3H), 5.28 (s,2H), 3.91 (s,3H), 3.43 (s,3H), 2.24 (s,3H), 0.28 (s,18H).
6	δ 7.67 (d,2H), 7.61 (m,2H), 7.44 (m,2H), 5.24 (q,2H), 3.88 (s,3H), 3.41 (s,3H), 2.21 (s,3H), 0.28 (s,18H).
7	δ 7.7 (d,1H), 7.53 (m,3H), 7.37 (m,3H), 7.20 (m,1H), 6.7 (broad d, 1H), 5.13 (s,2H), 3.94 (s,3H), 2.83 (d,3H), 2.21 (s,3H), 0.27 (s,9H).
9	δ 7.65 (s,1H), 7.53 (t,2H), 7.44 (d,1H), 7.3-7.4 (m,3H), 7.2 (d,1H), 6.7 (broad s,1H), 5.13 (s,2H), 3.95 (s,3H), 2.8 (d,3H), 2.21 (s, 3H), 0.39 (s,8H).
10	δ 7.7 (s,1H), 7.6 (d,1H), 7.5-7.6 (m,4H), 7.3-7.4 (m,6H), 7.2 (m,2H), 6.6-6.7 (broad s,1H), 5.11 (s,2H), 3.93 (s,3H), 2.8 (d, 3H), 2.17 (s, 3H), 0.55 (s,5.5 H).
11	δ 7.7 (s,1H), 7.6 (d,1H), 7.5-7.6 (m,2H), 7.3-7.4 (m,4H), 7.2 (d,1H), 6.7 (broad s,1H), 5.12 (s,2H), 3.95 (s,3H), 3.5 (q,2H), 2.85 (d,3H), 2.21 (s,3H), 0.95 (t,3H), 0.25 (s,6H).
12	δ 7.6 (d,2H), 7.5 (d,1H), 7.45 (d,3H), 7.3 (m,3H), 7.15 (d,1H), 5.15 (s,2H), 3.81 (s,3H), 3.68 (s,3H), 2.23 (s,3H), 0.38 s, 6.5H).
13	δ 7.6 (d,1H), 7.59 (d,2H), 7.5 (d,2H), 7.3-7.4 (m,2H), 7.15 (d,1H), 5.2 (s,2H), 3.81 (s,3H), 3.68 (s,3H), 2.23 (s,3H), 0.26 (s,7H).
14	δ 7.74 (d,1H), 7.59 (s,2H), 7.5-7.6 (m,2H), 7.34 (m,3H), 7.2 (d,1H), 5.16 (s,2H), 3.81 (s,3H), 3.68 (s,3H), 2.25 (s,3H), 0.28 (s,8H).
15	δ 7.7 (s,1H), 7.58 (d,1H), 7.55 (t,2H), 7.3-7.5 (m,3H), 7.2 (d,1H), 5.13 (s,2H), 4.03 (s,3H), 3.81 (s,3H), 2.21 (s,3H), 0.27 (s,7.4 H).

100

- 16 δ 7.6 (s,1H), 7.52 (t,2H), 7.4 (t,2H), 7.26-7.4 (m,3H), 7.1 (d,1H), 5.13 (s,2H), 4.03 (s,3H), 3.81 (s,3H), s.21 (s,3H), 0.39 (s,7H).
- 17 δ 7.70 (s,1H), 7.6 (d,1H), 7.51 (m,2H), 7.3-7.5 (m,3H), 7.2 (d,1H), 6.2-6.4 (q,1H), 6.0-6.1 (q,1H), 5.7-5.8 (q,1H), 5.13 (s,2H), 4.03 (s,3H), 3.81 (s,3H), 2.20 (s,3H), 0.35 (s,6H).
- 18 δ 7.7 (s,1H), 7.6 (d,1H), 7.5 (m,3H), 7.3 (t,1H), 7.2 (d,1H), 5.13 (t,2H), 4.03 (s,3H), 3.81 (s,3H), 2.21 (s,3H), 0.92 (t,3H), 0.75 (q,2H), 0.25 (s,5H).
- 20 δ 7.7 (s,1H), 7.6 (d,2H), 7.3-7.5 (m,12H), 7.2 (d,1H), 5.11 (s,2H), 4.03 (s,3H), 3.79 (s,3H), 2.17 (s,3H), 0.55 (s,5H).
- 21 δ 7.8 (s,1H), 7.6 (d,1H), 7.57 (s,1H), 7.4-7.5 (m,4H), 7.3-7.4 (m,6H), 7.2 (m,1H), 5.14 (s,2H), 3.79 (s,3H), 3.67 (s,3H), 2.21 (s,3H), 0.56 (s,6H).
- 22 δ 7.7 (s,1H), 7.5-7.6 (m,2H), 7.45 (d,1H), 7.3-7.4 (m,3H), 7.2 (d,1H), 5.16 (s,2H), 3.81 (s,3H), 3.68 (s,3H), 2.25 (s,3H), 0.39 (s,8H).
- 23 δ 7.6 (d,1H), 7.3-7.5 (m,2H), 7.2 (m,3H), 6.8 (d,1H), 4.95 (s,2H), 4.02 (s,3H), 3.83 (s,3H), 2.25 (s,3H), 0.34 (s,7H).
- 27 δ 8.53 (d,1H), 7.91 (s,1H), 7.60 (m,1H), 7.45 (m,2H), 7.34 (d,1H), 7.25 (m,1H), 5.33 (d,1H), 5.26 (d,1H), 3.89 (s,3H), 3.41 (s,3H), 2.29 (s,3H), 0.3 (s,9H).

^a ¹H NMR data are in ppm downfield from tetramethylsilane. Couplings are designated by (s)-singlet, (d)-doublet, (t)-triplet, (q)-quartet, (m)-multiplet, (dd)-doublet of doublets, (dt)-doublet of triplets, (br s)-broad singlet.

5 Test compounds were first dissolved in acetone in an amount equal to 3% of the final volume and then suspended at a concentration of 200 ppm in purified water containing 250 ppm of the surfactant Trem[®] 014 (polyhydric alcohol esters). The resulting test suspensions were then used in Tests A-F. Spraying these 200 ppm test suspensions to the point of run-off on the test plants is the equivalent of a rate of 500 g/ha.

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TEST A

The test suspension was sprayed to the point of run-off on wheat seedlings. The following day the seedlings were inoculated with a spore dust of *Erysiphe graminis* f. sp. *tritici*, (the causal agent of wheat powdery mildew) and incubated in a growth chamber at 20°C for 7 days, after which disease ratings were made.

TEST B

The test suspension was sprayed to the point of run-off on wheat seedlings. The following day the seedlings were inoculated with a spore suspension of *Puccinia recondita* (the causal agent of wheat leaf rust) and incubated in a saturated atmosphere at 20°C for 24 h, and then moved to a growth chamber at 20°C for 6 days, after which disease ratings were made.

TEST C

The test suspension was sprayed to the point of run-off on rice seedlings. The following day the seedlings were inoculated with a spore suspension of *Pyricularia oryzae* (the causal agent of rice blast) and incubated in a saturated atmosphere at 27°C for 24 h, and then moved to a growth chamber at 30°C for 5 days, after which disease ratings were made.

TEST D

The test suspension was sprayed to the point of run-off on tomato seedlings. The following day the seedlings were inoculated with a spore suspension of *Phytophthora infestans* (the causal agent of potato and tomato late blight) and incubated in a saturated atmosphere at 20°C for 24 h, and then moved to a growth chamber at 20°C for 5 days, after which disease ratings were made.

TEST E

The test suspension was sprayed to the point of run-off on grape seedlings. The following day the seedlings were inoculated with a spore suspension of *Plasmopara viticola* (the causal agent of grape downy mildew) and incubated in a saturated atmosphere at 20°C for 24 h, moved to a growth chamber at 20°C for 6 days, and then incubated in a saturated atmosphere at 20°C for 24 h, after which disease ratings were made.

TEST F

The test suspension was sprayed to the point of run-off on cucumber seedlings. The following day the seedlings were inoculated with a spore suspension of *Botrytis cinerea* (the causal agent of gray mold on many crops) and incubated in a saturated atmosphere at 20°C for 48 h, and moved to a growth chamber at 20°C for 5 days, after which disease ratings were made.

Results for Tests A-F are given in Table A. In the table, a rating of 100 indicates 100% disease control and a rating of 0 indicates no disease control (relative to the controls). A dash (-) indicates no test results. ND indicates disease control not determined due to phytotoxicity.

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Table A

<u>Cmpd No.</u>	<u>Test A</u>	<u>Test B</u>	<u>Test C</u>	<u>Test D</u>	<u>Test E</u>	<u>Test F</u>
1	97	100	86	63	44 ^a	81
2	100	100	91	64	99 ^a	0
3	100	100	90	0	33 ^a	44
4	94	100	99	86	61 ^a	0
5	85	97	53	0	5 ^a	44
6	91	84	0	0	0 ^a	0
7	100 ^a	100	97	-	93 ^a	ND
8	100 ^a	100	91	-	98 ^a	ND
9	100	100	94	97	100 ^a	0
10	97	100	53	86	100 ^a	0
11	100	100	74	77	100 ^a	0
12	100	98	32	0	97 ^a	0
13	100	99	86	47	98 ^a	0
14	99	100	94	46	96 ^a	84
15	100 ^a	100 ^a	78 ^b	-	100 ^a	-
16	100	100 ^a	97	97	100 ^a	67
17	100	100 ^a	94	92	96 ^a	0
18	100	100 ^a	97	85	93 ^a	1
19	94	100	94	0	68 ^a	0
20	100	100	94	92	98 ^a	74
21	97	100	53	75	87 ^a	0
22	99	100	90	20	49 ^a	0
23	100	100	97	0	60 ^a	0
24	99	99	29	0	0 ^a	0
25	99	99	86	61	16 ^a	89
26	100	100	53	0	27 ^a	71
27	100 ^a	100	90	-	92 ^a	39

^a The compound was sprayed at a concentration of 10 ppm (equivalent to 25 g/ha).

^b The compound was sprayed at a concentration of 40 ppm (equivalent to 100 g/ha).

TEST G5 Fall Armyworm

Test units, each consisting of a H.I.S. (high impact styrene) tray with 16 cells were prepared. Wet filter paper and approximately 8 cm² of lima bean leaf was placed into twelve of the cells. A 0.5-cm layer of wheat germ diet was placed into the four remaining cells. Fifteen to twenty third-instar larvae of fall armyworm (*Spodoptera frugiperda*) were placed into a 230-mL (8-ounce) plastic cup. Solutions of each of the

test compounds in 75:25 acetone-distilled water solvent were sprayed into the tray and cup. Spraying was accomplished by passing the tray and cup on a conveyer belt directly beneath a flat fan hydraulic nozzle which discharged the spray at a rate of 0.14 kilograms of active ingredient per hectare (about 0.14 pounds per acre) at 207 kPa (30 p.s.i.). The insects were transferred from the 230-mL cup to the H.I.S. tray (one insect per cell). The trays were covered and held at 27°C and 50% relative humidity for 48 hours, after which time readings were taken on the twelve cells with lima bean leaves. The four remaining cells were read at 6-8 days for delayed toxicity. Of the compounds tested, the following gave control efficacy levels of 80% or greater: 13, 21, and 22.

10

TEST H

Southern Corn Rootworm

Test units, each consisting of a 230-mL (8-ounce) plastic cup containing a 6.5-cm² (1-square-inch) plug of a wheatgerm diet, were prepared. The test units were sprayed as described in TEST G with individual solutions of the test compounds. After the spray on the cups had dried, five second-instar larvae of the southern corn rootworm (*Diabrotica undecimpunctata howardi*) were placed into each cup. The cups were held at 27°C and 50% relative humidity for 48 hours, after which time mortality readings were taken. The same units were read again at 6-8 days for delayed toxicity. Of the compounds tested, the following gave control efficacy levels of 80% or greater: 11, 19, and 22.

20

TEST I

Contact Test Against Black Bean Aphid

Individual nasturtium leaves were infested with 10 to 15 aphids (all morphs and growth stages of *Aphis fabae*) and sprayed with their undersides facing up as described in TEST G. The leaves were then set in 0.94-cm (3/8-inch) diameter vials containing 4 mL of sugar solution (approximately 1.4 g per liter) and covered with a clear plastic 29-mL (1-ounce) cup to prevent escape of the aphids that drop from the leaves. The test units were held at 27°C and 50% relative humidity for 48 hours, after which time mortality readings were taken. Of the compounds tested, the following gave mortality levels of 80% or higher: 21 and 22.

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TEST J

Two-Spotted Spider Mite

Pieces of kidney bean leaves, each approximately 6.5 cm² (1 square inch) in area, that had been infested on the undersides with 25 to 30 adult mites (*Tetranychus urticae*), were sprayed with their undersides facing up on a hydraulic sprayer with a solution of the test compound in 75:25 acetone-distilled water solvent. Spraying was accomplished by passing the leaves, on a conveyor belt, directly beneath a flat fan hydraulic nozzle which discharged the spray at a rate of 0.14 kilograms of active ingredient per hectare (about 0.14 pounds per acre) at 207 kPa (30 p.s.i.). The leaf squares were then placed

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underside-up on a square of wet cotton in a petri dish and the perimeter of the leaf square was tamped down onto the cotton with forceps so that the mites could not escape onto the untreated leaf surface. The test units were held at 27°C and 50% relative humidity for 48 hours, after which time mortality readings were taken. Of the
5 compounds tested, the following gave mortality levels of 80% or higher: 7, 10, 11, 13, 19, 21, 22, 24, and 25.

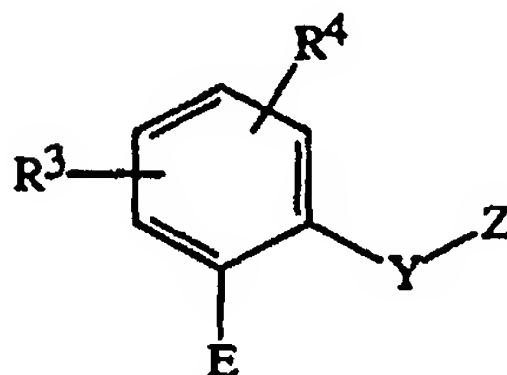
The same units were held an additional 5 days and read for larvicide/ovicide mortality and/or developmental effects. Of the compounds tested, the following gave activity levels of 80% or higher: 7, 11, and 23.

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CLAIMS

What is claimed is:

1. A compound selected from Formula I, *N*-oxides and agriculturally-suitable salts thereof,

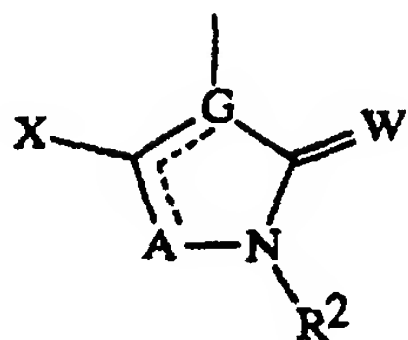
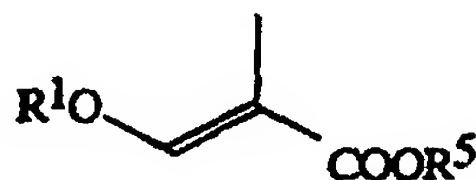
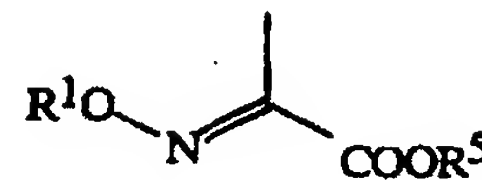
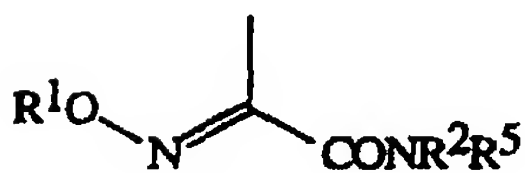
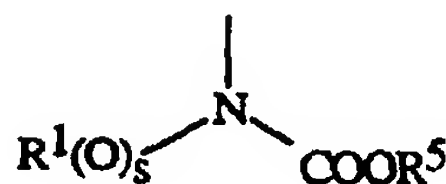
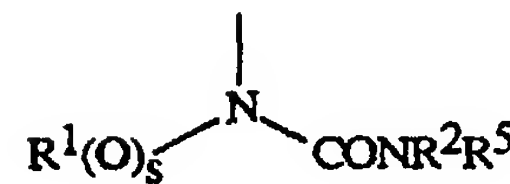


I

5

wherein:

E is

E¹E²E³E⁴E⁵E⁶

, or

A is O; S; N; NR⁵; or CR¹⁴;

10

G is C or N; provided that when G is C, A is O, S or NR⁵ and the floating double bond is attached to G; and when G is N, A is N or CR¹⁴ and the floating double bond is attached to A;

W is O; S; NH; N(C₁-C₆ alkyl); or NO(C₁-C₆ alkyl);X is OR¹; S(O)_mR¹; or halogen;

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R¹ and R⁵ are each independently H; C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₂-C₆ alkenyl; C₂-C₆ haloalkenyl; C₂-C₆ alkynyl; C₂-C₆ haloalkynyl; C₃-C₆ cycloalkyl; C₂-C₄ alkylcarbonyl; or C₂-C₄ alkoxy carbonyl;

R² is H; C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₂-C₆ alkenyl; C₂-C₆ haloalkenyl; C₂-C₆ alkynyl; C₂-C₆ haloalkynyl; C₃-C₆ cycloalkyl; C₂-C₄ alkylcarbonyl; C₂-C₄ alkoxy carbonyl; hydroxy; C₁-C₂ alkoxy; or acetyloxy;

20

R^3 and R^4 are each independently H; halogen; cyano; nitro; hydroxy; C_1 - C_6 alkyl; C_1 - C_6 haloalkyl; C_2 - C_6 alkenyl; C_2 - C_6 haloalkenyl; C_2 - C_6 alkynyl; C_2 - C_6 haloalkynyl; C_1 - C_6 alkoxy; C_1 - C_6 haloalkoxy; C_2 - C_6 alkenyloxy; C_2 - C_6 alkynyloxy; C_1 - C_6 alkylthio; C_1 - C_6 alkylsulfinyl; C_1 - C_6 alkylsulfonyl; formyl; C_2 - C_6 alkylcarbonyl; C_2 - C_6 alkoxycarbonyl; $NH_2C(O)$; $(C_1-C_4 \text{ alkyl})NHC(O)$; $(C_1-C_4 \text{ alkyl})_2NC(O)$; $Si(R^{13})_3$; $Ge(R^{13})_3$; $(R^{13})_3Si-C\equiv C-$; or phenyl, phenylethynyl, benzoyl, or phenylsulfonyl each substituted with R^9 and R^{10} ;

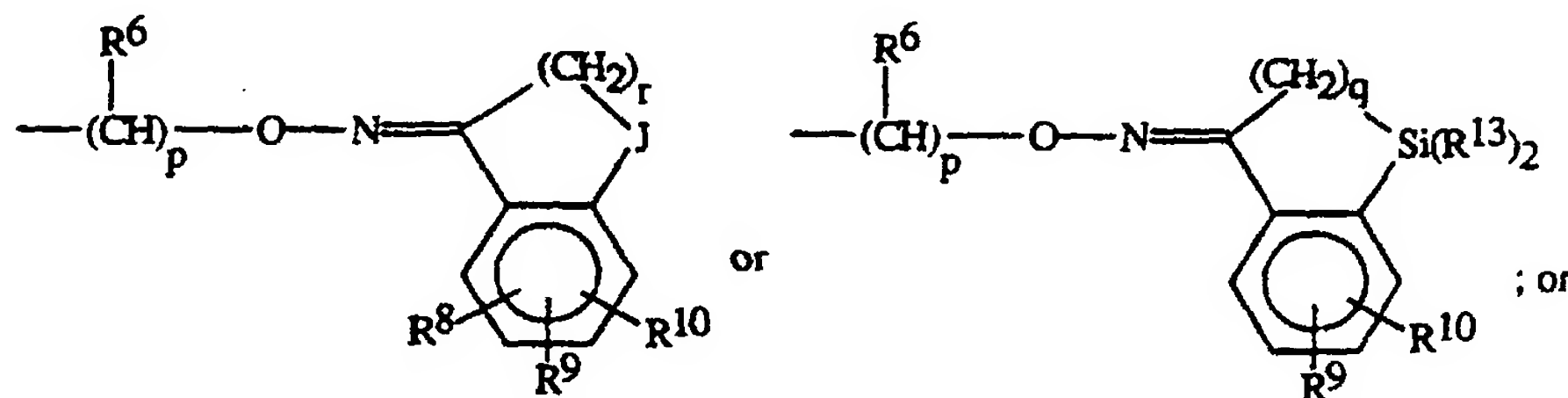
Y is $-O-$; $-S(O)_n-$; $-NR^6-$; $-C(=O)-$; $-CH(OR^6)-$; $-CHR^6-$; $-CHR^6CHR^6-$; $-CR^6=CR^6-$; $-C\equiv C-$; $-CHR^6O-$; $-OCHR^6-$; $-CHR^6S(O)_n-$; $-S(O)_nCHR^6-$; $-CHR^6O-N=C(R^7)-$; $-(R^7)C=N-OCH(R^6)-$; $-C(R^7)=N-O-$; $-O-N=C(R^7)-$; $-CHR^6OC(=O)N(R^{15})-$; or a direct bond; and the directionality of the Y linkage is defined such that the moiety depicted on the left side of the linkage is bonded to the phenyl ring and the moiety on the right side of the linkage is bonded to Z;

R^6 is independently H or C_1 - C_3 alkyl;

R^7 is H; C_1 - C_6 alkyl; C_1 - C_6 haloalkyl; C_1 - C_6 alkoxy; C_1 - C_6 haloalkoxy; C_2 - C_6 alkenyl; C_2 - C_6 haloalkenyl; C_2 - C_6 alkynyl; C_2 - C_6 haloalkynyl; C_3 - C_6 cycloalkyl; C_2 - C_4 alkylcarbonyl; C_2 - C_4 alkoxycarbonyl; cyano; or morpholinyl;

Z is phenyl substituted with R^8 , R^9 , and R^{10} ; or Z is a 5 to 14-membered aromatic heterocyclic ring system selected from the group monocyclic ring, fused bicyclic ring and fused tricyclic ring, each aromatic ring system containing 1 to 6 heteroatoms independently selected from the group nitrogen, oxygen, and sulfur, provided that each aromatic ring system contains no more than 4 nitrogens, no more than 2 oxygens, and no more than 2 sulfurs, each aromatic ring system substituted with R^8 and optionally substituted with one of R^9 , R^{10} , or both R^9 and R^{10} ; or

Y and Z are taken together to form

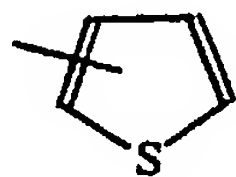


R^3 , Y, and Z are taken together with the phenyl ring to form a naphthalene moiety substituted on either ring with R^8 and on either ring with R^4 ;

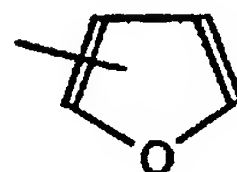
- J is $-\text{CH}_2-$; $-\text{CH}_2\text{CH}_2-$; $-\text{OCH}_2-$; $-\text{CH}_2\text{O}-$; $-\text{SCH}_2-$; $-\text{CH}_2\text{S}-$; $-\text{N}(\text{R}^{16})\text{CH}_2-$; or $-\text{CH}_2\text{N}(\text{R}^{16})-$; each CH_2 group optionally substituted with 1 to 2 CH_3 ;
 R^8 is $\text{SiR}^{19}\text{R}^{20}\text{R}^{21}$ or $\text{GeR}^{19}\text{R}^{20}\text{R}^{21}$;
 R^9 is H; 1-2 halogen; C_1 - C_6 alkyl; C_1 - C_6 haloalkyl; C_1 - C_6 alkoxy; C_1 - C_6 haloalkoxy; C_2 - C_6 alkenyl; C_2 - C_6 haloalkenyl; C_2 - C_6 alkynyl; C_1 - C_6 alkylthio; C_1 - C_6 haloalkylthio; C_1 - C_6 alkylsulfinyl; C_1 - C_6 alkylsulfonyl; C_3 - C_6 cycloalkyl; C_3 - C_6 alkenyloxy; $\text{CO}_2(\text{C}_1$ - C_6 alkyl); $\text{NH}(\text{C}_1$ - C_6 alkyl); $\text{N}(\text{C}_1$ - C_6 alkyl) $_2$; $-\text{C}(\text{R}^{18})=\text{NOR}^{17}$; cyano; nitro; SF_5 ; $\text{SiR}^{22}\text{R}^{23}\text{R}^{24}$; or $\text{GeR}^{22}\text{R}^{23}\text{R}^{24}$; or R^9 is phenyl, benzyl, benzoyl, phenoxy, pyridinyl, pyridinyloxy, thienyl, thienyloxy, furanyl, pyrimidinyl, or pyrimidinyloxy each substituted with R^{11} and R^{12} ;
 R^{10} is H; halogen; C_1 - C_4 alkyl; C_1 - C_4 haloalkyl; C_1 - C_4 alkoxy; nitro; or cyano; or R^{11} and R^{12} are each independently H; halogen; C_1 - C_4 alkyl; C_1 - C_4 haloalkyl; C_1 - C_4 alkoxy; C_1 - C_4 haloalkoxy; nitro; cyano; $\text{Si}(\text{R}^{13})_3$; or $\text{Ge}(\text{R}^{13})_3$;
 R^{13} is independently C_1 - C_4 alkyl;
 R^{14} is H; halogen; C_1 - C_6 alkyl; C_1 - C_6 haloalkyl; C_2 - C_6 alkenyl; C_2 - C_6 haloalkenyl; C_2 - C_6 alkynyl; C_2 - C_6 haloalkynyl; or C_3 - C_6 cycloalkyl;
 R^{15} , R^{16} , R^{17} , and R^{18} are each independently H; C_1 - C_3 alkyl; or phenyl optionally substituted with halogen, C_1 - C_4 alkyl, C_1 - C_4 haloalkyl, C_1 - C_4 alkoxy, C_1 - C_4 haloalkoxy, nitro or cyano;
 R^{19} , R^{20} , R^{21} , R^{22} , R^{23} , and R^{24} are each independently C_1 - C_6 alkyl; C_1 - C_6 alkenyl; C_1 - C_4 alkoxy; or phenyl;
m and n are each independently 0, 1 or 2;
p, r, and s are each independently 0 or 1; and
q is 1 or 2;
provided that when E is E^4 and Y is $-\text{O}-$; $-\text{S}(\text{O})_n-$; $-\text{NR}^6-$; $-\text{C}(=\text{O})-$; $-\text{CH}(\text{OR}^6)-$; $-\text{CHR}^6-$; $-\text{CHR}^6\text{CHR}^6-$; $-\text{CR}^6=\text{CR}^6-$; $-\text{C}\equiv\text{C}-$; $-\text{CHR}^6\text{O}-$; $-\text{OCHR}^6-$; $-\text{CHR}^6\text{S}(\text{O})_n-$; or $-\text{S}(\text{O})_n\text{CHR}^6-$, then R^8 is $\text{GeR}^{19}\text{R}^{20}\text{R}^{21}$.
2. A compound of Claim 1 wherein:
W is O when E is E^1 ;
 R^1 is C_1 - C_3 alkyl or C_1 - C_3 haloalkyl;
 R^2 is H; C_1 - C_3 alkyl; C_1 - C_3 haloalkyl; or cyclopropyl;
 R^3 and R^4 are each independently H; halogen; cyano; nitro; C_1 - C_6 alkyl; C_1 - C_6 haloalkyl; C_1 - C_6 alkoxy; or C_1 - C_6 haloalkoxy;
Y is $-\text{O}-$; $-\text{CH}=\text{CH}-$; $-\text{CH}_2\text{O}-$; $-\text{OCH}_2-$; $-\text{CH}_2\text{S}(\text{O})_n-$; $-\text{CH}_2\text{O}-\text{N}=\text{C}(\text{R}^7)-$; $-\text{C}(\text{R}^7)=\text{N}-\text{O}-$; $-\text{CH}_2\text{OC}(\text{O})\text{NH}-$; or a direct bond;
 R^7 is H; C_1 - C_6 alkyl; C_1 - C_6 haloalkyl; C_2 - C_6 alkenyl; C_2 - C_6 alkynyl; C_3 - C_6 cycloalkyl; or cyano;

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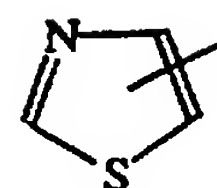
Z is phenyl substituted with R^8 , R^9 , and R^{10} ; or Z is



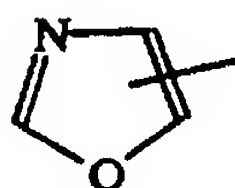
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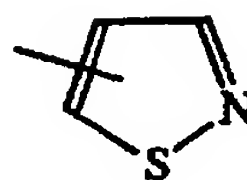
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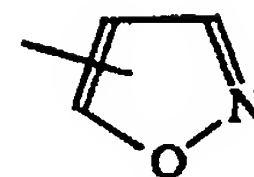
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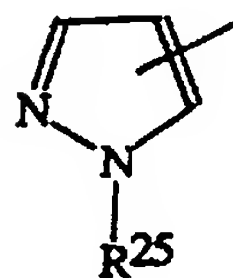
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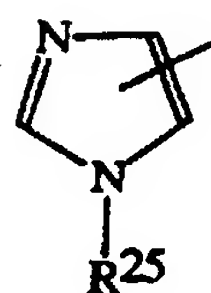
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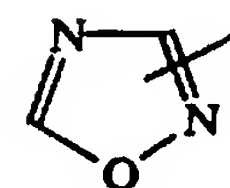
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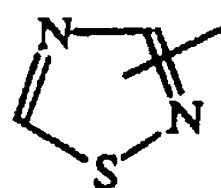
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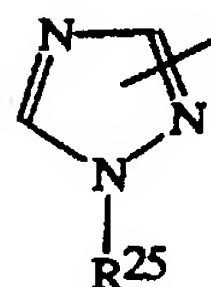
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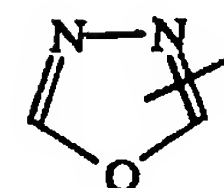
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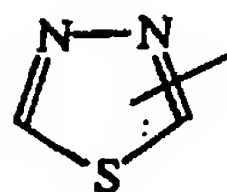
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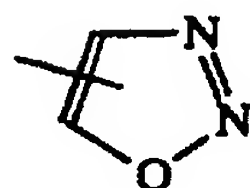
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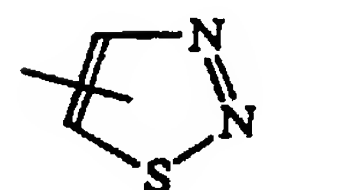
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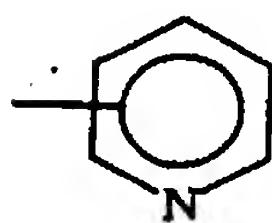
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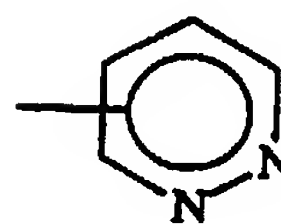
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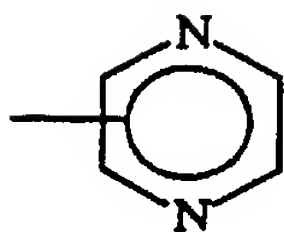


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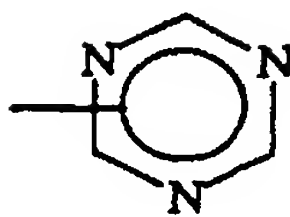


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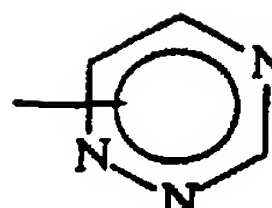
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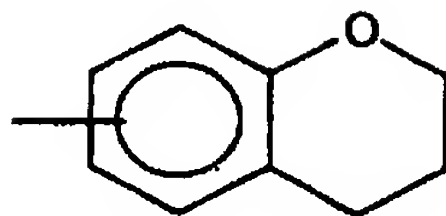
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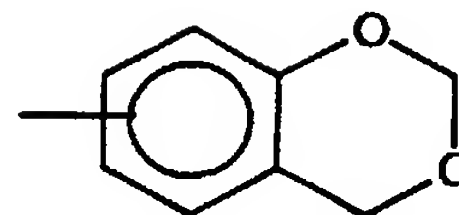
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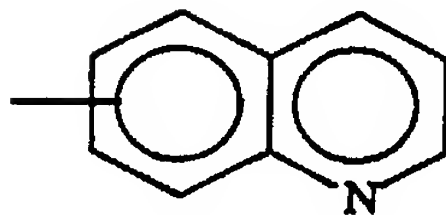
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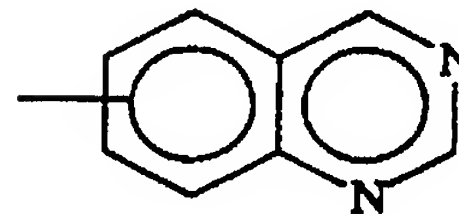
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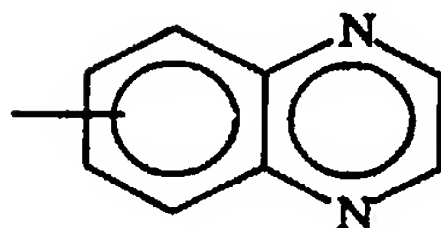
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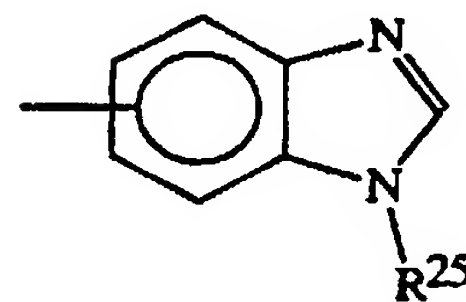
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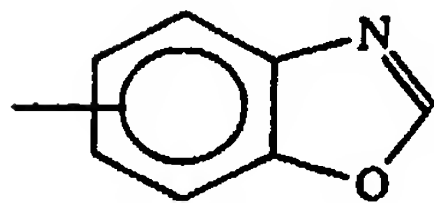
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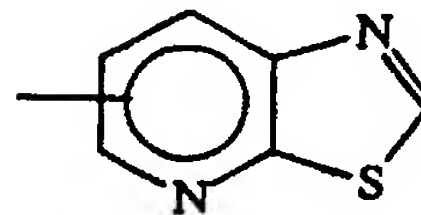
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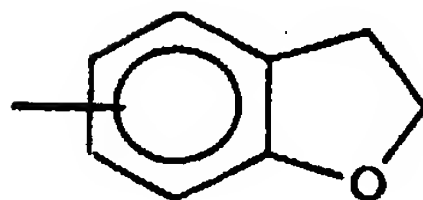
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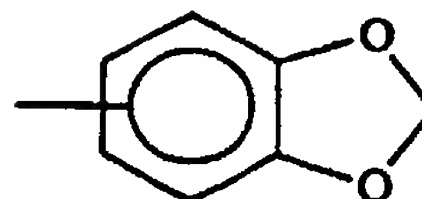
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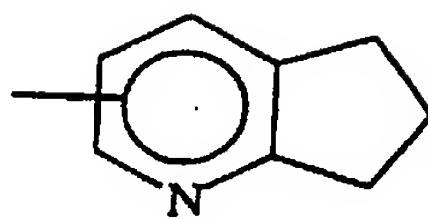


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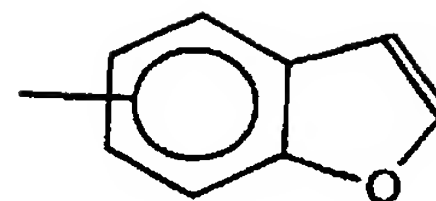


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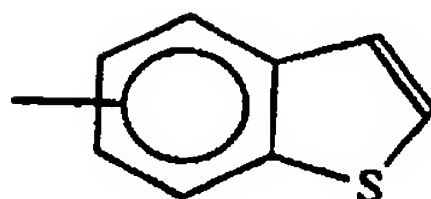
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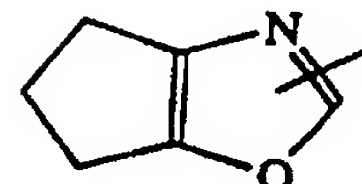
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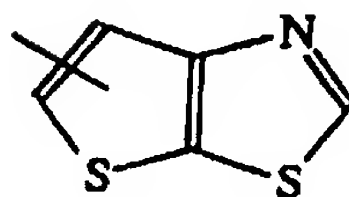
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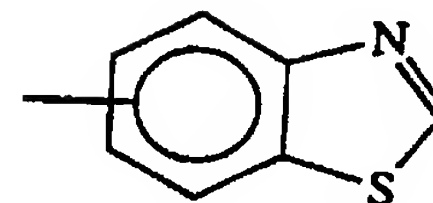


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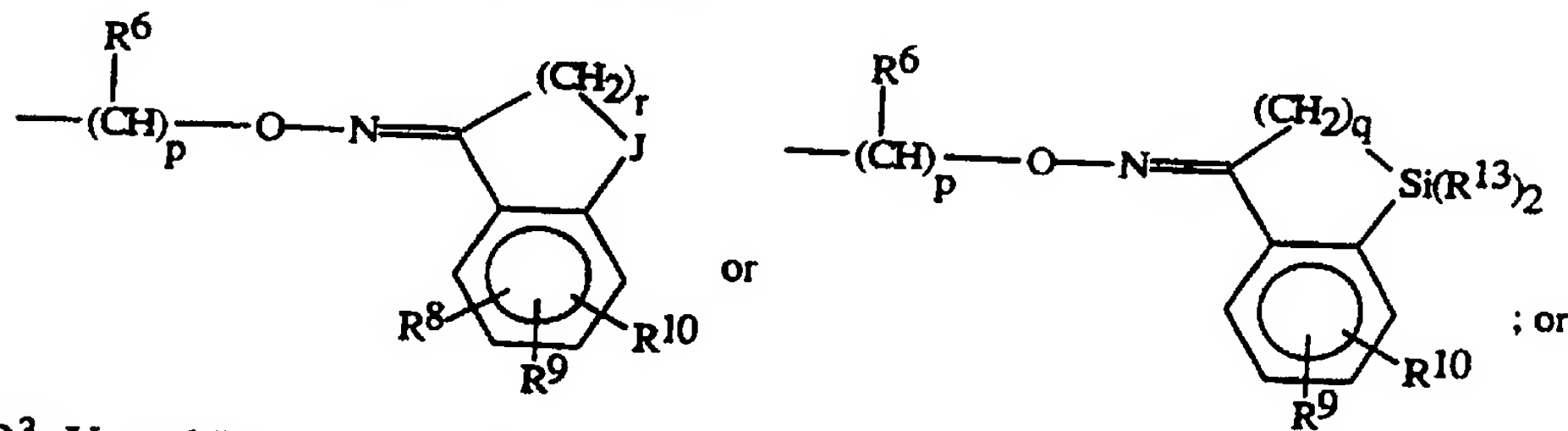
Z-36

or



Z-37

each group substituted with R^8 and optionally substituted with one of R^9 , R^{10} , or both R^9 and R^{10} ; or
Y and Z are taken together to form



5

R^3 , Y, and Z are taken together with the phenyl ring to form a naphthalene moiety substituted on either ring with R^8 and with a floating R^4 ;

R^9 is H; 1-2 halogen; C_1 - C_6 alkyl; C_1 - C_6 haloalkyl; C_1 - C_6 alkoxy; C_1 - C_6 haloalkoxy; C_1 - C_6 alkylthio; C_3 - C_6 cycloalkyl; CO_2 (C_1 - C_6 alkyl); NH (C_1 - C_6 alkyl); N (C_1 - C_6 alkyl) $_2$; cyano; $SiR^{22}R^{23}R^{24}$; or $GeR^{22}R^{23}R^{24}$; or R^9 is phenyl, phenoxy, pyridinyl, pyridinyloxy, pyrimidinyl, or pyrimidinyloxy each optionally substituted with R^{11} and R^{12} ; and

10

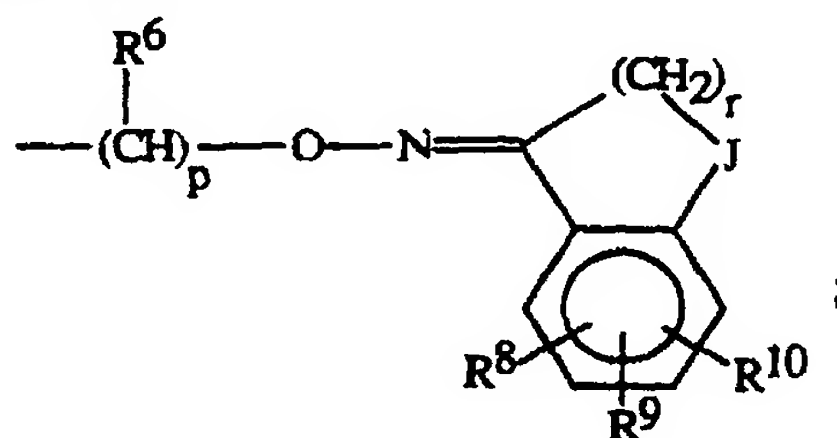
R^{25} is H; C_1 - C_6 alkyl; C_1 - C_6 haloalkyl; or phenyl optionally substituted with halogen, C_1 - C_4 alkyl, C_1 - C_4 haloalkyl, C_1 - C_4 alkoxy, C_1 - C_4 haloalkoxy, nitro or cyano.

15

3. A compound of Claim 2 wherein:

Z is phenyl substituted with R^8 , R^9 , and R^{10} ; or Z is Z-1 to Z-21, each substituted with R^8 and optionally substituted with one of R^9 , R^{10} , or both R^9 , and R^{10} ;
or

Y and Z are taken together to form



5

J is $-\text{CH}_2-$ or $-\text{CH}_2\text{CH}_2-$;

p is 0; and

r is 1.

4. A compound of Claim 3 wherein:

10 when E is E^1 , then A is O; N; NR^5 ; or CR^{14} ; and X is OR^1 ;

R^1 is C_1 - C_3 alkyl;

R^2 is H or C_1 - C_2 alkyl;

R^3 and R^4 are each H;

Y is $-\text{O}-$; $-\text{CH}=\text{CH}-$; $-\text{CH}_2\text{O}-$; $-\text{OCH}_2-$; $-\text{CH}_2\text{O}-\text{N}=\text{C}(\text{R}^7)-$; or $-\text{CH}_2\text{OC}(=\text{O})\text{NH}-$;

15

R^7 is H; C_1 - C_3 alkyl; or C_1 - C_3 haloalkyl; and

Z is phenyl substituted with R^8 , R^9 , and R^{10} ; or Z is Z-16, Z-18, or Z-1, each substituted with R^8 and optionally substituted with one of R^9 , R^{10} or both R^9 and R^{10} .

5. A compound of Claim 4 wherein:

20

E is E^1 ;

A is O or NR^5 ;

G is C;

Y is $-\text{O}-$; $-\text{CH}_2\text{O}-$; $-\text{OCH}_2-$; or $-\text{CH}_2\text{O}-\text{N}=\text{C}(\text{R}^7)-$; and

R^7 is H; C_1 - C_2 alkyl; or C_1 - C_2 haloalkyl.

25

6. A compound of Claim 4 wherein:

E is E^1 ;

A is N or CR^{14} ;

G is N;

Y is $-\text{O}-$; $-\text{CH}_2\text{O}-$; $-\text{OCH}_2-$; or $-\text{CH}_2\text{O}-\text{N}=\text{C}(\text{R}^7)-$;

30

R^7 is H; C_1 - C_2 alkyl; or C_1 - C_2 haloalkyl.

7. A compound of Claim 3 wherein:

E is E^2 , E^3 , E^4 , E^5 , or E^6 .

8. A compound of Claims 3 through 7 wherein:

R¹ is methyl;

R² is methyl; and

Z is phenyl substituted with R⁸, R⁹, and R¹⁰.

9. The compound of Claim 4 which is selected from the group:

- 5 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-(trimethylsilyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3*H*-1,2,4-triazol-3-one;
- methyl α -(methoxyimino)-2-[[2-methyl-4-(trimethylgermyl)phenoxy]methyl]benzeneacetate;
- 10 methyl 2-[[[1-[3-(dimethylphenylsilyl)phenyl]ethylidene]amino]oxy]methyl]- α -(methoxyimino)benzeneacetate;
- methyl α -(methoxyimino)-2-[[[1-[3-(trimethylgermyl)phenyl]ethylidene]amino]oxy]methyl]benzeneacetate; and
- 15 methyl α -(methoxyimino)-2-[[[1-[3-(trimethylsilyl)phenyl]ethylidene]amino]oxy]methyl]benzeneacetate.

10. A fungicidal composition comprising a fungicidally effective amount of a compound of Claim 1 and at least one of a surfactant, a solid diluent or a liquid diluent.

11. A method for controlling plant diseases caused by fungal plant pathogens comprising applying to the plant or portion thereof, or to the plant seed or seedling, a
20 fungicidally effective amount of a compound of Claim 1.

12. An arthropodocidal composition comprising an arthropodocidally effective amount of a compound of Claim 1 and at least one of a surfactant, a solid diluent or a liquid diluent.

13. A method for controlling arthropods comprising contacting the arthropods or
25 their environment with an arthropodocidally effective amount of a compound of Claim 1.

INTERNATIONAL SEARCH REPORT

International Application No
PC, /US 95/15236

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07F7/08 A01N55/00 C07F7/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07F A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO,A,94 26700 (CIBA-GEIGY AG) 24 November 1994 see the whole document and particularly page 34, example I.225 ---	1-13
Y	EP,A,0 398 692 (SHIONOGI SEIYAKU KK) 22 November 1990 cited in the application see pages 31, 36 and 37, and claims ---	1-13
Y	EP,A,0 596 692 (SHIONOGI SEIYAKU KK) 11 May 1994 cited in the application see page 3, line 37 and claims ---	1-13
-/--		

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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Date of the actual completion of the international search

20 March 1996

Date of mailing of the international search report

27.03.96

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INTERNATIONAL SEARCH REPORT

Inter mal Application No
PCT/US 95/15236

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 433 233 (DR. R. MAAG AG) 19 June 1991 cited in the application see table 3, compounds 98 and 130 -----	1-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PC., US 95/15236

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		EP-A- 0651737	10-05-95
		HU-A- 69038	28-08-95
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		NO-A- 950168	17-03-95
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